

**GROUND-WATER CONTAMINATION BY CRUDE OIL**

**AT THE BEMIDJI, MINNESOTA, RESEARCH SITE:**

**U.S. GEOLOGICAL SURVEY TOXIC WASTE—GROUND-WATER CONTAMINATION STUDY**

Papers presented at the Toxic-Waste Technical Meeting,  
Tucson, Arizona, March 20-22, 1984

Marc F. Hult, Editor

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**GEOLOGICAL SURVEY**

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## Preface

Ground-water contamination by toxic organic substances is a pressing national problem. In recent years it has become increasingly clear that a large proportion of contamination problems result from the discharge and entrainment into moving ground water of liquid organic substances. These liquids may enter the subsurface owing to spills, leakage from storage and disposal containers, and deliberate discharges. The volume of the subsurface that becomes contaminated by constituents that are dissolved or otherwise entrained in ground water may be much larger than that containing the liquid source. A better scientific understanding of how organic fluids move and are dissolved by ground water is needed for accurate predictions of contaminant behavior and effective remedies.

In 1982, the U.S. Geological Survey began a national thrust program on ground-water contamination and toxic waste (Ragone, S. E., 1984, Toxic waste—ground-water contamination program, fiscal year 1983: U.S. Geological Survey Open-File Report 84-474). One major part of the program is interdisciplinary research conducted at field research sites. A crude-oil spill near Bemidji, Minnesota was proposed by the Minnesota District and selected by the Office of Hazardous Waste Hydrology for study focusing on the behavior of organic fluids in the subsurface. Two other national research sites are in Cape Cod, Massachusetts, and Pensacola, Florida, where ground water has been contaminated by sewage and wood-preserving chemicals, respectively.

Preliminary field work during the summer of 1983 confirmed that the Bemidji site was suitable for the intended study. These preliminary results and research plans were presented at a meeting sponsored by the Office of Hazardous Waste Hydrology in Tucson, Arizona, March 20-22, 1984.

This report contains the papers presented at the technical meeting in Tucson that relate to the Bemidji project. Separate additional reports present the results at the Cape Cod research site (U.S. Geological Survey, 1984, Movement and fate of solutes in a plume of sewage-contaminated ground water, Cape Cod, Massachusetts: LeBlanc, D. R., ed., U.S. Geological Survey Open-File Report 84-475), the Pensacola research site (U.S. Geological Survey, 1984, Movement and fate of creosote waste in ground water: Mattraw, Jr., H. C., and Franks, B. J., eds., U.S. Geological Survey Open-File Report 84-466) and other research related to the hydrology of hazardous wastes being conducted by the Geological Survey.

The overall objectives of the research conducted at the Bemidji site are to obtain a more complete understanding of the mobilization, transport, and fate of petroleum derivatives in the shallow subsurface and to use this understanding to develop predictive models of contaminant behavior. The papers presented at the meeting give a

broad overview of the studies being conducted by the researchers from the U.S. Geological Survey and academic institutions that are working together to achieve these objectives. The papers are in the order in which they were presented at the conference by the first author and deal, in succession, with hydrogeologic, chemical, and biologic research elements. Some planned and ongoing research activities that are at an early stage were not represented by papers. These include study of the migration of volatile constituents through the unsaturated zone and study of the nature and behavior of non-ideal solutes such as micelles and emulsions. Geophysical research being used to define the geologic framework and petroleum distribution was presented at an earlier session of the meeting.

Results of the Bemidji project will have substantial transfer value to many similar problems. The first paper points out attributes of the site that make it well suited for long-term, interdisciplinary research, describes the contaminant source, and provides a summary of the hydrogeologic setting.

Mathematical modeling will be needed to simulate the many physical, chemical, and biologic processes that govern contaminant behavior. The second paper suggests an approach to identifying the most important interactions, processes, and dimensions, and reducing them to a tractable mathematical problem. The emphasis is on developing and applying techniques to simulate movement and alteration of a lighter-than-water fluid phase near the water table and determining how this phase acts as a source of gaseous and dissolved constituents to the unsaturated and saturated zones.

The rate of petroleum dissolution is a critical, poorly understood process controlling contamination of the saturated zone. The third paper describes the physical basis for exchange processes between the petroleum source, water, and gas. Novel analysis of published data indicates that the rate of oil-to-water exchange (dissolution) is independent of ground-water velocity at the flow rates that prevail at the site.

Once contaminants have been dissolved and are moving through the saturated zone, contaminant movement is controlled by advective and dispersive solute transport. The fourth paper explores the relationship between hydraulic conductivity and dispersivity and suggests ways to quantify them by field measurement of hydraulic conductivity in three dimensions and at several scales.

For the purpose of modeling movement of the crude oil as a separate fluid phase, the oil at the site can be considered to be a single, nearly homogeneous fluid. However, the oil contains many individual compounds that behave in widely different ways once removed from the bulk oil phase and migrating through the porous media as vapors or solutes. Moreover, as constituents are selectively removed from the oil, the bulk phase will change in composition. The fifth paper documents selective removal of low-

molecular-weight aliphatic hydrocarbons in the contaminants that have migrated down the hydraulic gradient.

At present, there are no methods approved by the U.S. Geological Survey for analysis of crude oil, of water samples contaminated by crude oil (one-phase), or of two-phase samples of water and oil, although numerous analytical methods have been published and are in widespread use. The sixth paper describes methods that could be developed for use by the Survey's Central Laboratory system.

The natural geochemistry of the ground-water system is dominated by inorganic chemical constituents. The seventh paper describes a project to study the effect of the organic contaminants on inorganic sediment-water interaction. Important processes occurring might include changes in the ability of the porous media to sorb petroleum derivatives, release of trace constituents and nutrients necessary for biodegradation, and modification of the rate of aquifer dissolution.

A large proportion of the crude oil consists of compounds that can be degraded by bacteria under aerobic conditions. Moreover, dissolution of the crude oil may be a biologically mediated process. The eighth paper presents a preliminary description of indigenous bacteria in uncontaminated aquifer material near the spill site and outlines plans for additional research on microbial process under both aerobic and anaerobic conditions. Bacteria capable of degrading the petroleum were found. The rates of petroleum degradation probably are severely limited by availability of oxygen and nutrients.

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**CHAPTER A**  
**GROUND-WATER CONTAMINATION BY CRUDE OIL AT**  
**THE BEMIDJI, MINNESOTA RESEARCH SITE—**  
**AN INTRODUCTION**

By M. F. Hult<sup>1</sup>

**ABSTRACT**

The U.S. Geological Survey has begun a research project to improve understanding of the mobilization, transport, and fate of petroleum contaminants in the shallow subsurface and to use this understanding to develop predictive models of contaminant behavior.

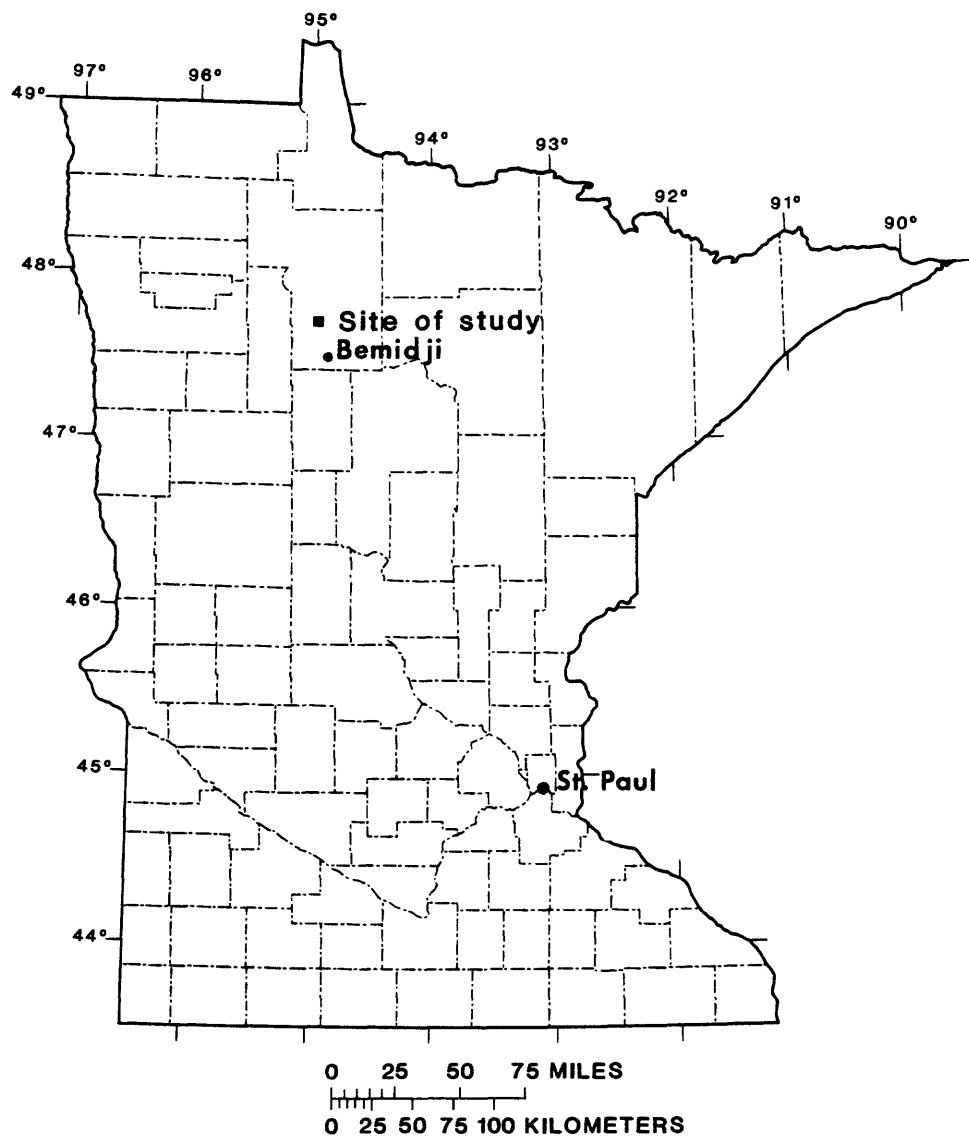
The project site is near Bemidji in northern Minnesota where an accidental spill of 10,500 barrels of crude oil occurred when a pipeline broke on August 20, 1979. Regulatory and remedial actions have been completed. The site is in a remote area with neither man-made hydraulic stresses nor other anthropogenic sources of the compounds of interest. The spill is in the recharge area of a local flow system that discharges to a small closed lake approximately 1,000 feet down the hydraulic gradient. The aquifer is pitted outwash dissected by younger glacial channels and is underlain by poorly permeable till at a depth of about 80 feet. Ground water dissolves oil floating on the water table under the spill site and moves toward the lake. At the water table, ground water enters the lake through lacustrine sediments; at depth, flow may be underneath the lake through the outwash. Contaminant transport has been as rapid as 4 feet per day based on the rate of movement of contaminants monitored through wells installed within a few days of the spill, but average rates are undoubtedly much less.

**INTRODUCTION**

A field research study is being conducted by the U.S. Geological Survey that involves interdisciplinary research on the movement and fate of petroleum in the shallow subsurface. The research site is in a sparsely populated area near Bemidji in northern Minnesota, where 10,500 barrels of petroleum (crude oil) was accidentally spilled on August 20, 1979, because of a break in a pipeline (fig. 1). Although about 7,800 barrels of the petroleum were removed after the spill, and clean up has been completed, sufficient petroleum remains in the subsurface for scientific study.

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**Figure 1.--Location of research site near Bemidji, Minnesota.**

### Purpose and Scope

The overall objectives of the project are to obtain a more complete understanding of the mobilization, transport, and fate of petroleum derivatives in the unsaturated zone and in ground water and to use this understanding to develop predictive models. Research by several different teams within the U.S. Geological Survey, and in conjunction with academic institutions, contribute to this overall goal. This paper describes the site and the contaminant source in a general way in order to provide a context for the more detailed, interpretive papers that follow.

### Sources of Information

Field work by the U.S. Geological Survey at the site began in May 1983. This initial field work verified that the site was suitable for the intended research, and improved the understanding of the local hydrology and geology work. Samples were collected for preliminary analysis and interpretation by individual researchers.

A major source of information for this paper is data collected by Lakehead Pipe Line Company, Inc. in the course of evaluating and minimizing the effects of the spill. Information obtained from August through November 1979 are presented and interpreted by Pfannkuch (1979). Other information specifically about the spill site are from the files of the MPCA (Minnesota Pollution Control Agency), from an unpublished thesis (Eames, 1981) and from discussions with Dr. Pfannkuch and with State and company representatives. Photographs were useful in documenting events and conditions immediately after the spill and during initial cleanup. Information on the regional setting is from the published reports cited and from unpublished data in the files of the U.S. Geological Survey.

### Acknowledgments

The cooperation and interest of Mr. Thomas Gray (Lakehead Pipe Line Company, Inc.), Mr. Leonard Bergstrom (Beltrami County), is gratefully acknowledged.

### PHYSICAL SETTING

The site is located in a sparsely populated area in north-central Minnesota approximately 11 miles northwest of Bemidji (fig. 1). The pipeline break itself occurred in the SE $\frac{1}{4}$  of SW $\frac{1}{4}$ , sec. 2, T.147 N., R.35 W.

### Land Use and Access

The contaminated area and adjacent land is owned by the State and Beltrami County. There are no dwellings or other buildings within 1 mile. The land is not suitable for agriculture; forest products are of little economic value at present. The major land use is recreational (primarily hunting). Access to the area is along the pipeline right-of-way, which parallels adjacent railroad tracks. The area of the spill can be reached by passenger vehicle during the summer and by snowmobile during the winter.

## Climate

Temperature and precipitation are measured at the Bemidji airport (located 9 miles southeast of the site) and published by the National Oceanic and Atmospheric Administration, 1982. Normal (1941-70) annual temperature is 3°C; monthly normal temperatures range from -16°C in January to 20°C in July. Normal annual precipitation is 22.25 inches. Only 3.23 inches normally falls during the period November through March when the ground is frozen, but most of it is stored as snowpack and is available for recharge of ground water during spring melt. Nearly half the precipitation (10.48 inches) occurs during June, July, and August when evapotranspiration is highest.

## Surface Water

The research site is located in the headwaters of the Mississippi River, approximately 1 mile south of the subcontinental divide at which drainage is northerly to Hudson Bay. Local drainage is to the northeast toward a small, unnamed lake located approximately 1,000 feet from the pipeline rupture and toward small, swamp-filled depressions (fig. 2).

## HYDROGEOLOGY

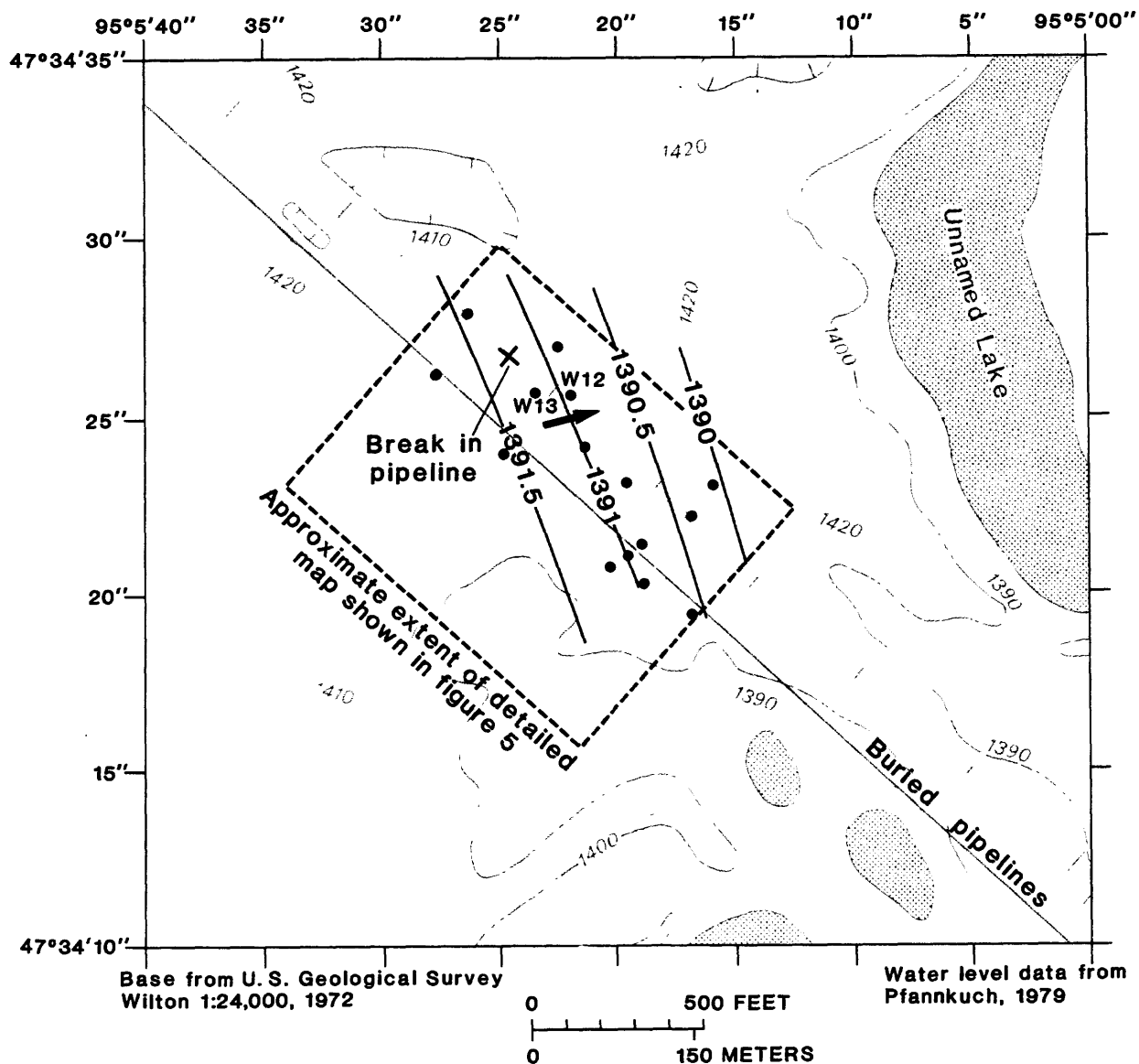
The site was chosen in part because the local hydrogeology is relatively simple. The ground-water flow at the water table is characteristic of the local flow systems that develop around lakes in outwash aquifers. However, because of the detailed research to be conducted, much additional information, at varying scales, will be needed to characterize flow at depth and in the immediate vicinity of the petroleum-water contact. Within the plume of dissolved constituents, the hydraulic conductivity of the aquifer will need to be defined in three dimensions (Miller, Chapter D).

## Geology and Water-Bearing Characteristics

The site is located on the Bagley outwash plain within the Bemidji physiographic area (Wright, 1972). The outwash is bounded to the north by the Bigstone Moraine of the St. Louis sublobe of the Des Moines lobe, and on the west and south by the Itasca Moraine of the Wadena lobe (Hobbs and Goebel, 1982). The pitted outwash plain has been mapped by Oakes and Bidwell (1968) as consisting of predominantly medium to coarse sand. The outwash is dissected by gravel-filled channels that are now partly occupied by ice-block lakes. Regionally, the drift is more than 400 feet thick and is underlain by crystalline bedrock (Oakes and Bidwell, 1968).

Figure 3 shows a generalized hydrogeologic section across the spill area and to the lake northeast of the site. Geologic data used to construct the section are from the test holes shown, from additional shallow test holes near the line of section, and from a core taken of the lake sediments (not shown). Samples were collected in test holes by the U.S. Geological Survey at approximately 5-foot intervals using a split-spoon sampler.

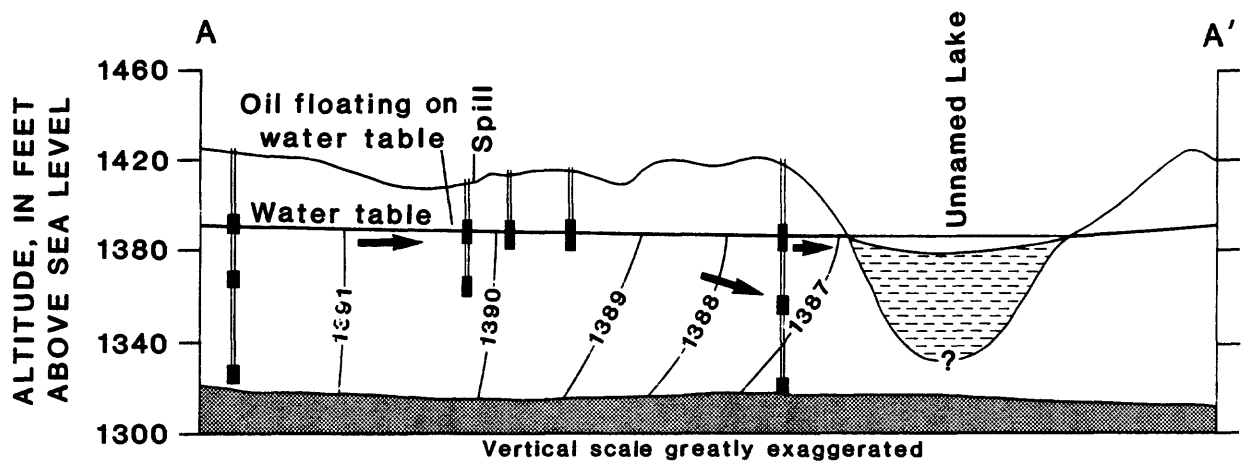
The predominant geologic unit is a brown to buff, variably sorted, medium grained, calcareous, quartz-rich sand. Particle-size analyses, laboratory



### EXPLANATION

- |        |  |     |   |
|--------|--|-----|---|
| —1420— | Topographic contour, interval 10 feet. National Geodetic Vertical Datum of 1929                              | W12 | Observation well. Number denotes well referred to in text     |
| —1391— | Approximate water-table contour, September 1979. Interval 0.5 foot. National Geodetic Vertical Datum of 1929 | →   | Approximate direction of ground-water flow at the water table |







**Figure 2.--Configuration of the water table, September 1979.**



Location of section shown on figure 4

0 500 FEET

### EXPLANATION

-  Organic sediments
-  Outwash
-  Till
-  -1389- Line of equal hydraulic head. Contour interval 1 foot
-  Generalized direction of ground-water flow
-  Cluster of wells used for hydrologic control. Thickness of interval open to well bore exaggerated for clarity

**Figure 3.--Generalized hydrogeologic section.**

permeability, and percent organic carbon for shallow samples in the immediate vicinity of the pipeline break are shown in table 1. Siegel and Franzi (1984, Chapter G) provide additional sedimentologic and mineralogic data. These analyses show that the outwash is relatively uniform. However, excavations and test holes at the site have shown that the outwash also contains beds of gravel and layers of silt. The silt layers are distinct and can be mapped using ground-penetrating radar (Olhoeft and others, written commun., 1984).

**Table 1.—Particle-size distribution, permeability, and percent organic carbon of selected outwash samples from test hole near pipeline break (modified from Eames, 1981)**

	Depth of sample				
	2 2/2 - 3 1/2 ft	12 1/2 - 13 1.2 ft	20 - 21 ft	10 - 11 ft	Surface
Mean particle size, $\phi$ units	0.77	1.86	3.59	0.92	1.65
Median particle size ( $\phi_{50}$ ), $\phi$ units	1.2	1.79	3.42	1.38	1.67
Effective particle size ( $\phi_{10}$ ), $\phi$ units	3.1	2.7	5.1	2.67	2.65
Inclusive Graphic Standard Deviation, $\phi$ units	1.49	0.60	1.02	1.37	1.12
Laboratory Permeability (ft/day)	96	83	4.1	120	57
Organic matter percent by weight	4.3	0.2	0.3	0.3	—

Approximately 80 feet below land surface, the outwash is underlain by a gray, calcareous, clay-rich till that is plastic in texture. The till is uniform in composition and appearance at each location and depth sampled, and is presumed to be areally extensive. Similar till elsewhere in Minnesota has a

vertical hydraulic conductivity of about  $3 \times 10^{-4}$  feet/day. Shallow coring showed that the lake basin contains up to 35 feet of organic deposits. Near the shore, the upper part of the deposits are fibrous and contain abundant remains of terrestrial and emergent aquatic vegetation. In the center of the lake, the water-sediment interface is indistinct and sediments consist primarily of gyttja (peat-like deposits).

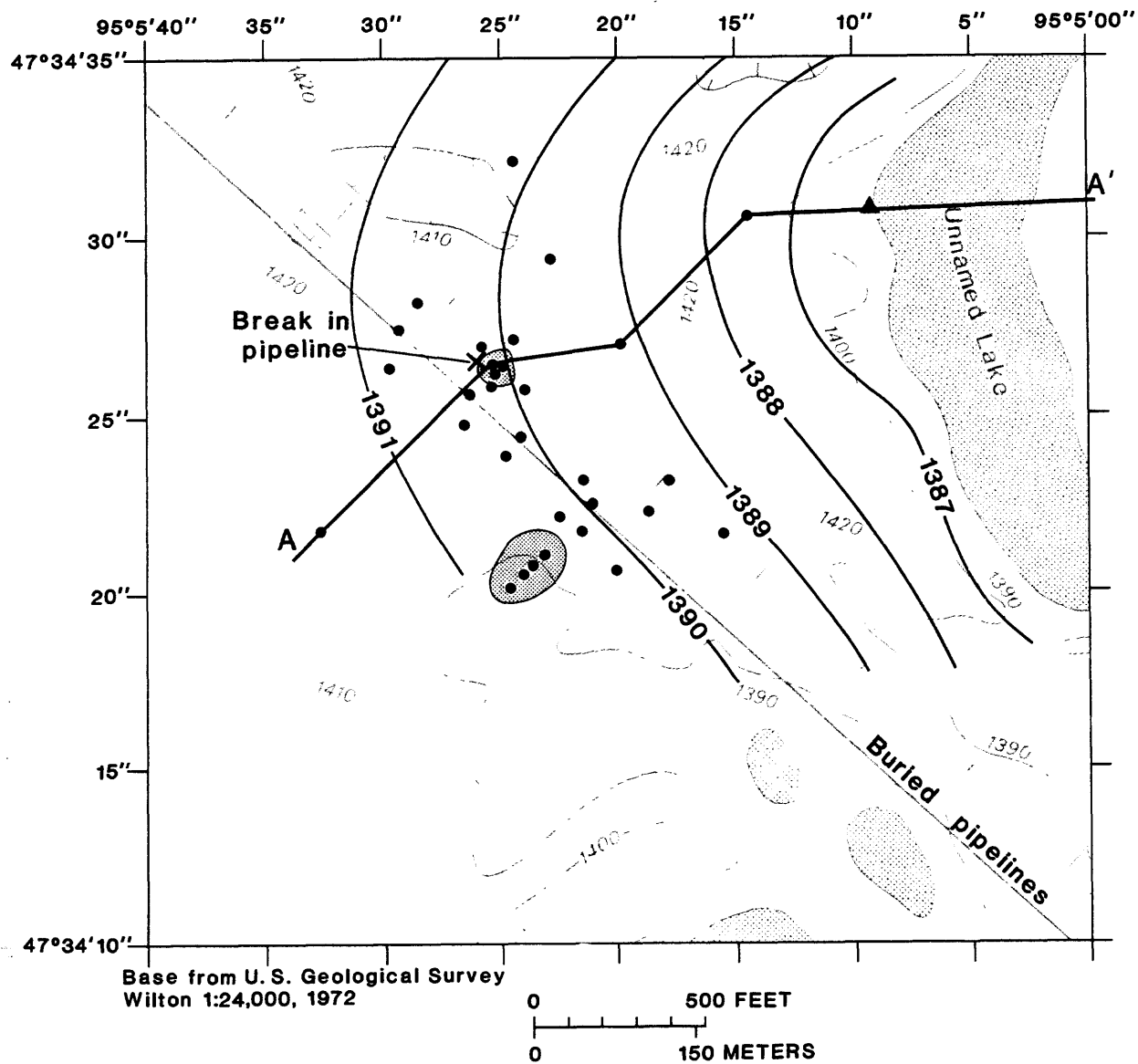
### Direction of Ground-Water Flow

Immediately after the spill, the configuration of the water table was determined based on measurements in 15 observation wells (fig. 2). During the period from August 30 to October 15, 1979, water-table contours were essentially parallel to the lake edge. The hydraulic gradient was approximately 0.003. Subsequent measurements by the U.S. Geological Survey in a greater number of wells (fig. 4) shows the same configuration. Because water levels in individual wells fluctuated together in a systematic way during the period and because there are no nearby artificial hydraulic stresses such as pumping wells, it is likely that the direction of ground-water flow past the site of spill has not changed markedly with time. The hydraulic gradient may change significantly seasonally if surface-water runoff to the lake raises water levels in the lake quickly compared to rise in the water table.

The hydrogeologic section (fig. 3) also shows the vertical distribution of hydraulic head and the general direction of flow along the line of section. Wells completed at the water table are constructed with screens 5 feet long with the water level in the well at the approximate mid-point of the screen at the time of installation. Wells completed below the water table are constructed with screens 2 feet long and are grouted in place with neat grout to prevent vertical flow around the casing. At the well cluster farthest upgradient, there usually is less than 0.1 foot of head difference between wells. At the well cluster farthest down the hydraulic gradient, near the lake, the water level in the deepest well usually is about 1 foot lower than the water table. The data indicate that one significant stream line (flow path) enters the lake at the water table through the organic sediments. Other stream lines originating near the spill may go underneath the lake. This implies that part of the dissolved contaminants may follow a local flow system to the organic deposits where they are sorbed, and part may be advancing through an intermediate flow system beneath the lake.

### CONTAMINANT CHEMISTRY

Crude oil and petroleum products are major sources of ground-water contamination. Fumes from volatile constituents may explode if they accumulate in basements and sewers. Dissolved constituents may impart objectionable taste and odors to water; taste and odor thresholds are as low as 50 ug/L for some individual constituents of petroleum. Some compounds, such as benzene, toluene, and xylene, are readily soluble in water, mobile in the hydrogeologic environment, and toxic. Higher molecular-weight aromatic compounds, such as polynuclear aromatic hydrocarbons, are less mobile. However, some of these are carcinogenic or otherwise toxic at trace concentrations. Proposed guidelines for potable water are as low as a few nanograms per liter for some individual carcinogenic compounds.



### EXPLANATION

- |        |  |      |   |
|--------|--|------|---|
| —1420— | Topographic contour, interval 10 feet. National Geodetic Vertical Datum of 1929                            |      | Approximate extent of oil floating on water table |
| —1390— | Approximate water-table contour, September 1983. Interval 1 foot. National Geodetic Vertical Datum of 1929 | •    | Observation well                                  |
|        |  | ▲    | Staff gage  |
|        |  | A—A' | Trace of hydrogeologic section                    |

**Figure 4.--Configuration of the water table, September 1983.**

### Summary of Petroleum Spill and Cleanup

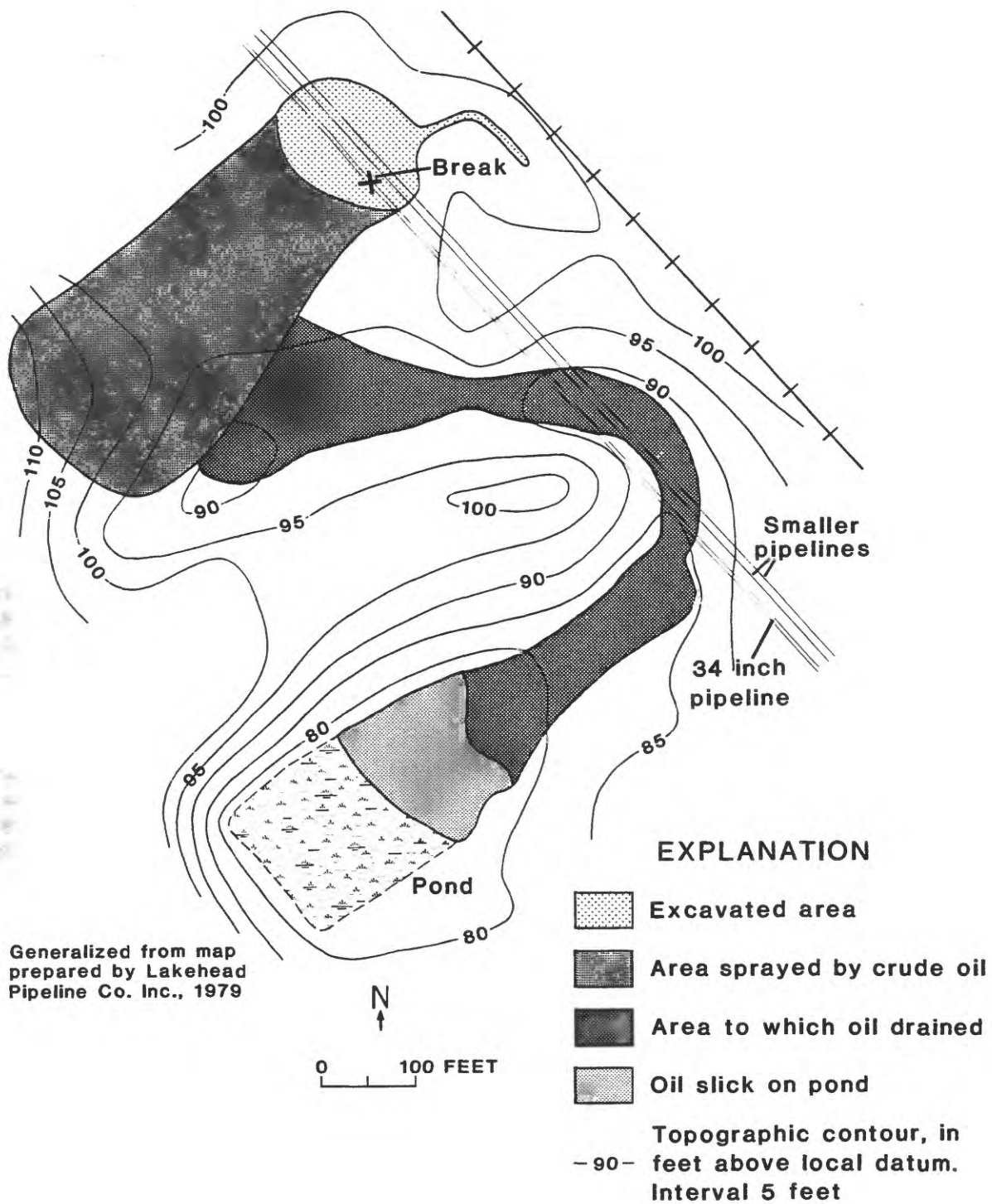
On August 20, 1979, at 9:45 a.m., a buried, 34-inch-diameter pipeline operating at approximately 500 pounds per square inch pressure burst. The high pressure in the pipeline caused petroleum to be sprayed over an area of approximately 70,000 square feet (fig. 5). Some of this oil drained off and collected in topographic depressions. The area over and to which the oil drained was approximately 22,000 square feet. Some oil reached a small pond and created an oil slick that was removed by trenching and pumping. A pool of oil approximately 75 feet in diameter and 2 feet deep formed at the point of rupture. Of the estimated 10,500 barrels (58,000 ft<sup>3</sup>) that was spilled, approximately 6,600 barrels (37,000 ft<sup>3</sup>) was pumped up and removed from the site by August 23, 1979. Approximately 800 barrels were burned or evaporated, and 500 barrels excavated and treated by land-farming (Eames, 1981). During the spring of 1980, contaminated soil with an average of 2 percent oil by weight was spread to a thickness of 6 to 8 inches along the pipeline right of way, fertilized, and planted with brome grass.

### Distribution and Movement of the Petroleum Source

Petroleum is present at the site in the unsaturated zone, as a distinct fluid phase floating on the water table, and as constituents dissolved in ground water. The unsaturated zone is about 15 feet thick at the location of the pipeline break and from 0 to 40 feet thick regionally. The area over which the unsaturated zone was affected by downward percolation from the spill was mapped in detail immediately following the spill (figs. 3 and 5). In most of this area, the petroleum penetrated only a few inches and is now (1984) visible as dark staining of the sand grains. Virtually all the petroleum that is mobile as a distinct fluid phase has reached the water table.

Petroleum percolated rapidly through the outwash sand after the spill. Within 2 days, at least 8 inches had accumulated on the water table. Cores obtained in 1983 showed that there are two separate areas, approximately 500 feet apart, where there is about 1 foot of oil on the water table (fig. 4). The oil seems to be uniform in composition as indicated by measurements of specific gravity, gas chromatography, and visual appearance. The oil will continue to migrate down the hydraulic gradient until the remaining volume is insufficient for continued movement as a macroscopically distinct fluid phase as discussed by Pollock (Chapter B).

The volume of aquifer either partially or fully saturated with petroleum continues to act as a source of contamination to the ground-water system. Some compounds in petroleum are not readily degraded by bacteria and are sparingly soluble in water. It is likely that a defineable source of these compounds and resulting plume in the ground water will persist for decades. However, preliminary field and laboratory work strongly suggests that a large part of the petroleum consists of light aliphatic compounds that are being volatilized (Baedecker and others, Chapter E). A large part of the petroleum compounds can be degraded by indigenous bacteria under aerobic conditions (Chang and Ehrlich, Chapter H).



**Figure 5.--Topography and Areal extent of contamination at land surface.**

The areal extent and concentration of petroleum present as dissolved constituents of ground water has changed rapidly and reversibly with time. Figure 6 shows the concentration of oil and grease (measured by freon extraction) in fluid from well W13 for the period August 1979 to October 1981. Well W13 is the well that has persistently shown the highest concentrations and is located nearest the rupture. After an initial rapid rise in concentrations owing to the first arrival of contaminants, concentration decreased sharply during the fall and winter of 1979-80. The concentration rose again in 1980 and continued to decline through 1981. The initial decline may have been due to rapid dissolution of the most soluble constituents in contact with the water, and the subsequent, short-lived increases may be due to remobilization during water-table fluctuations and recharge events (Pfannkuch, Chapter C).

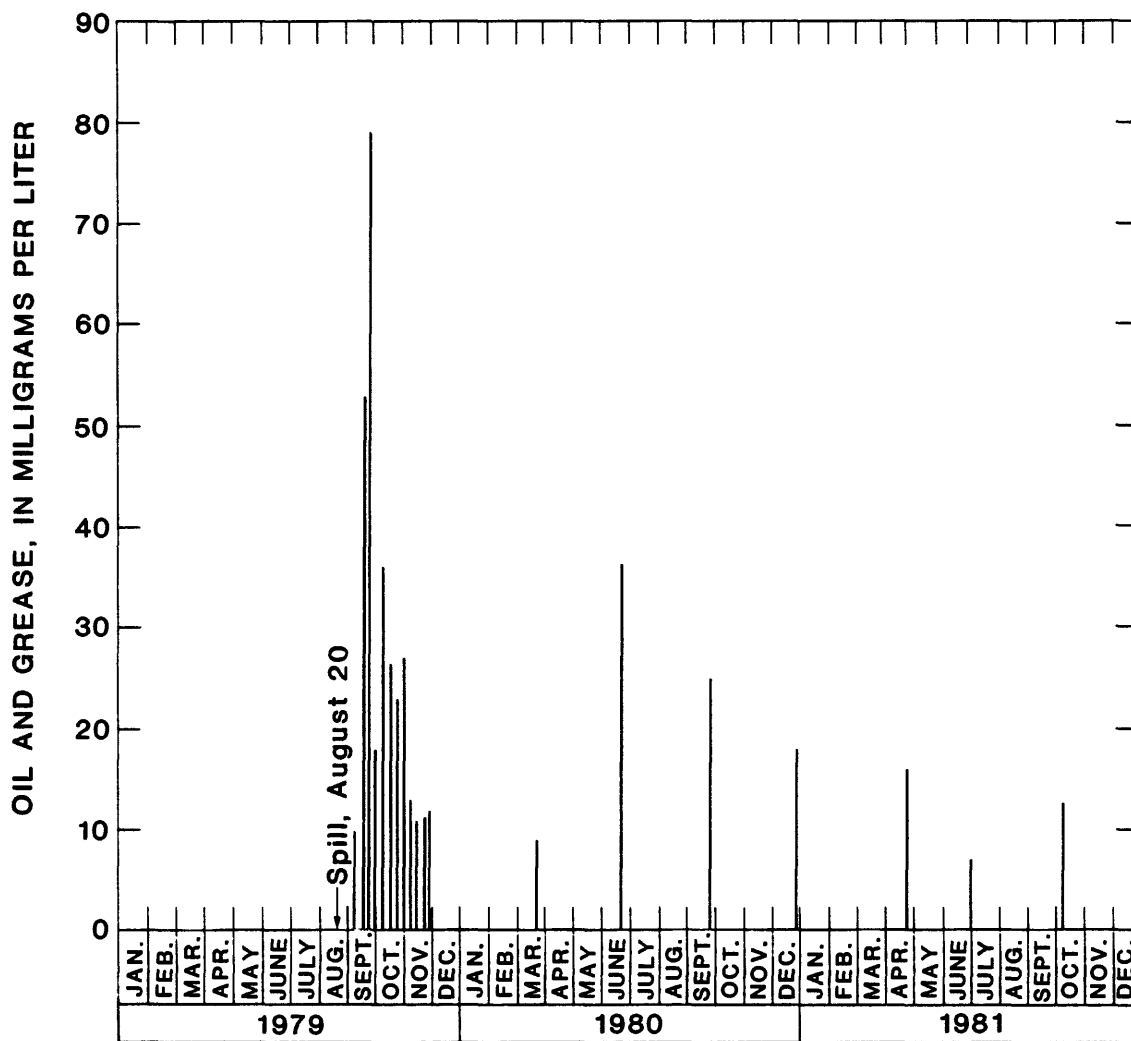
Data from other wells, such as W12, show similar changes (table 2). Pfannkuch (1979) used the difference between the time of arrival of peak concentrations at W13 and W12 to estimate a ground-water velocity of 4 feet per day. This velocity, however, seems high compared to calculations of ground-water velocities from estimates of hydraulic conductivity (table 1), porosity, and hydraulic gradient. Perhaps, as Pfannkuch suggests, the first arrivals are dominated by movement through the most permeable zones that the seemingly periodic nature of variations in concentrations is due to periodic recharge, and that the long-term decline is due to a reduction in source-strength.

## SUMMARY

A field research site near Bemidji, Minnesota, is being developed where interdisciplinary research is being conducted to obtain a more complete understanding of the mobilization, transport, and fate of petroleum contaminants in the shallow subsurface. This understanding will be used to develop predictive models of contaminant behavior. This paper summarizes the hydrogeology of the site and the nature of the contaminant source and provides a context for subsequent papers in this volume.

The hydrogeologic and geochemical framework of the sites is relatively simple. The contaminant source is at an accidental spill of 10,500 barrels of crude oil that occurred on August 20, 1979. Clean-up efforts recovered about 6,500 barrels. Approximately 1,300 barrels were burned, land farmed, or evaporated. Regulatory and remedial action have been completed.

The site is in a remote area with neither man-made hydraulic stresses nor other anthropogenic sources of the compounds of interest. The spill is in the recharge area of a local flow system that discharges to a small closed lake approximately 1,000 feet down the hydraulic gradient. The aquifer is characteristic of pitted outwash dissected by younger glacial channels and is underlain by poorly permeable till at a depth of about 80 feet. One flow path apparently goes through the oil floating on the water table to the lake where ground water enters through lacustrine sediments. Other stream lines originating near the source may go beneath the lake. Contaminant transport has been as rapid as 4 feet/day based on the rate of movement of contaminants monitored in wells installed within a few days of the spill, but average rates are probably less.



**Figure 6.--Concentration of oil and grease in fluid from monitoring well W13, 1979-81.**

Table 2.—Concentration of oil and grease in monitoring wells, August 29, 1979 to October 5, 1981 (Data from Lakehead Pipe Line Company, Inc.).

Date	Local well number																
	W9	W10	W11	W12	W13	W14	W15	W16	W17	W18	W19	W20	W21	W25	W26	W27	
8/29/79	37	41	16	4.7	-	34	71	-	-	-	-	-	-	-	-	-	
9/9/79	2.3	2.4	-	1.0	10	3.0	3.6	2.5	7.9	3.0	2.4	1.8	2.4	-	-	-	
9/16/79	4.7	3.1	-	4.3	53	4.0	79	3.2	14	3.5	2.8	3.1	7.6	-	-	-	
9/23/79	6.2	9.3	6.3	1.9	79	2.1	88	17	4.9	6.4	2.1	5.1	6.8	-	-	-	
9/30/79	4.4	2.9	4.2	9.7	18	2.1	24	14	7.0	5.3	3.6	5.1	4.4	-	-	-	
10/7/79	6.5	2.2	6.1	16	36	11	14	14	21	5.7	3.7	3.5	3.1	-	-	-	
10/15/79	5.4	3.9	23	1.6	26	6.9	53	2.5	3.2	4.5	3.3	3.0	7.1	-	-	-	
10/23/79	4.1	4.1	5.3	1.4	23	3.3	37	2.7	5.2	4.0	2.6	2.7	5.5	-	-	-	
10/29/79	5.2	3.4	5.8	8.0	27	2.8	36	15	12	5.9	2.2	3.2	7.0	-	-	-	
11/7/79	5.1	5.0	9.8	1.4	13	10	17	2.1	6.0	5.2	2.8	1.8	4.8	-	-	-	
11/13/79	6.2	4.5	4.8	1.0	11	6.0	17	1.0	3.1	4.2	3.0	2.7	5.2	-	-	-	
11/19/79	5.3	2.6	18	2.8	13	1.5	25	2.4	4.5	6.1	3.1	3.1	6.7	-	-	-	
11/26/79	3.7	5.4	13	2.6	15	8.9	34	1.8	3.8	4.5	3.4	2.1	3.2	-	-	-	
1/2/80	-	-	-	-	-	1.9	92	-	-	-	3.0	-	-	8.7	16	47	
3/26/80	-	4.0	-	1.7	9.2	-	24	-	-	3.3	4.4	-	-	-	-	23	
5/6/80	-	-	-	-	-	-	-	-	-	-	-	-	-	15	9.6	-	
6/25/80	-	3.9	-	9.6	36	-	8.9	-	-	12	4.2	-	-	13	12	11	
9/28/80	-	6.5	-	3.1	25	-	42	-	-	7.0	3.5	-	-	9.4	6.8	7.7	
12/29/80	-	5.0	-	14	18	-	16	-	-	-	1.5	-	-	8.6	6.5	6.4	
4/29/81	-	3.3	-	<1.0	16	-	23	-	-	-	<1.0	-	-	<1.0	<1.0	<1.0	
7/1/81	-	3.0	-	3.6	7.0	-	2.8	-	-	-	2.6	-	-	3.4	1.6	4.1	
10/5/81	-	3.4	-	5.3	9.2	-	11	-	-	-	3.4	-	-	13	5.2	5.2	

Petroleum is present at the site in the unsaturated zone, as a distinct fluid phase floating on the water table, and as constituents dissolved in ground water. The unsaturated zone is about 15 feet thick in the area of the spill and from 0 to 40 feet thick regionally. The area over which the unsaturated zone was affected by downward percolation from the spill was mapped in detail immediately following the spill. In most of this area, the petroleum penetrated only a few inches and is now (1984) visible as dark staining of the sand grains. Virtually all the petroleum that is mobile as a distinct fluid phase has reached the water table.

Petroleum percolated rapidly through the outwash sand after the spill. Within 2 days, at least 8 inches had accumulated on the water table. Core samples obtained in 1983 showed that there are two separate areas, approximately 500 feet apart, where there is about 1 foot of oil on the water table. The oil is essentially uniform in composition and will continue to migrate down the hydraulic gradient until the remaining volume is insufficient for continued movement as a macroscopically distinct fluid phase.

The volume of aquifer either partially or fully saturated with petroleum continues to act as a source of contamination to the ground-water system. Petroleum contains compounds such as polynuclear aromatic hydrocarbons that are not readily degraded by bacteria, are sparingly soluble in water, and that are believed to be hazardous at concentrations as low as a few nanograms per liter. It is likely that a defineable source and resulting plume in the ground water of these compounds will persist for decades. However, preliminary field and laboratory work strongly suggests that a large part of the petroleum consists in light aliphatic compounds that are being volatilized and degraded by bacteria.

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**CHAPTER B**  
**USE OF COMPUTER SIMULATION FOR EVALUATING THE MOVEMENT**  
**OF PETROLEUM IN THE SHALLOW SUBSURFACE**

By David W. Pollock<sup>1</sup>

**ABSTRACT**

The transport of spilled petroleum in the shallow subsurface occurs by a complex combination of fluid flow, gaseous diffusion, and advective and dispersive transport in ground water. Although it is possible in principle to develop comprehensive mathematical models integrating the effects of all these transport processes, such models may be impractical to apply on a small enough scale to provide adequate resolution for many aspects of petroleum spills. An alternative approach is to analyze the overall transport by studying the component processes separately. These processes include fluid flow (petroleum, water, and air), transport of petroleum constituents in the unsaturated zone, and solute transport in the saturated zone. This approach has several potential applications to the Bemidji field site.

**INTRODUCTION**

When petroleum enters the subsurface it tends to move as a separate and distinct phase. However, small but significant amounts of most petroleum components dissolve in and are transported with ground water that comes in contact with the petroleum. Petroleum also contains volatile components that evaporate and move through the unsaturated zone. Consequently, to understand the fate of petroleum in the subsurface requires a quantitative understanding of multiphase flow and chemical transport, as well as the basic chemical and biological processes that affect petroleum.

Immediately after petroleum is spilled at or near land surface it begins to move downward through the unsaturated zone under the influence of gravity. Although the petroleum moves primarily downward, it also spreads laterally due to capillary forces. As the petroleum moves through the unsaturated zone, some is left behind, distributed in discontinuous pockets that are nearly immobile. Petroleum is less dense than water and begins to spread laterally when it reaches the water table. The petroleum first spreads outward in all directions from the region of accumulation below the spill and then continues to move on the water table under the influence of the hydraulic gradient. Throughout the process of infiltration and spreading, the volume swept by the petroleum increases until eventually all the petroleum is deposited in the porous medium resulting in a volume containing immobile, residual petroleum.

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However, the potential contamination problems associated with petroleum spills involve many more than those related directly to the movement of petroleum as a separate phase. The extent of petroleum migration as a separate fluid phase is relatively small in comparison with the area of potential contamination due to solute transport in the saturated zone and volatile transport in the unsaturated zone. However, the distribution of the petroleum fluid is critical in determining its characteristics as a source for ground-water contamination and volatiles in the unsaturated zone.

This report outlines the major transport processes associated with petroleum spills in the subsurface and presents some possible strategies and approaches for analyzing these processes quantitatively using mathematical models and computer simulation.

### **COMPUTER SIMULATION**

For a system as complex as a petroleum spill, computer simulation using mathematical models of fluid flow and chemical transport provides the only practical means of accounting for the interacting physical, chemical, and biological processes that affect petroleum in the subsurface. The theory of multiphase flow and multicomponent transport has been highly developed by the petroleum industry (Marle, 1981), and computer simulation has been used for nearly 20 years to analyze such phenomena in petroleum reservoirs (Crichlow, 1977; Aziz and Settari, 1979). Until recently, however, quantitative studies of the multiphase-flow aspects of petroleum spills have not included simulation (van Dam, 1967).

It is possible in principle to develop a comprehensive model accounting for all the interacting transport phenomena. However, such a model would be impractical to apply on a small enough scale to adequately describe many of the important aspects of petroleum spills. As a first approximation, overall transport can be analyzed by studying the component processes separately:

1. Fluid flow (petroleum, water, and air).
2. Transport of volatiles and dissolved constituents in the unsaturated zone.
3. Transport of dissolved petroleum constituents in the saturated zone.

### **Fluid Flow**

Infiltration and spreading of spilled petroleum can be studied using multiphase-flow theory to describe the simultaneous flow of petroleum, water, and air. The theory of multiphase flow in porous media is based on three basic assumptions: (1) different fluids may coexist at any point in the porous medium, (2) at any point the pressure within each fluid is related to its relative abundance, or degree of saturation at that point, and (3) the flow of a fluid phase is governed by a generalized form of Darcy's law in which the mobility (or hydraulic conductivity) is a function of the degree of saturation for the fluid in question. These assumptions result in a set of three partial differential flow equations, one for each phase. If the gas pressure is

constant, the analysis can be simplified so that only the flow of petroleum and water need be considered. The resulting set of equations can be solved using standard numerical techniques such as finite-difference or finite-element methods.

Multiphase-flow simulations will allow detailed study of characteristics of the petroleum-water displacement process and the resulting zones of contact between petroleum and water. The three-dimensional aspects of infiltration and spreading can be approximated best by considering a two-dimensional vertical cross section in cylindrical coordinates. This type of simulation can be used to examine the effects of such things as: (1) characteristics of the porous medium that influence transport (intrinsic permeability, porosity, and capillary characteristics), (2) layering, (3) antecedent moisture conditions in the unsaturated zone, (4) water-table fluctuations, and (5) physical properties of the petroleum such as density and viscosity. A sensitivity analysis of this kind will be extremely valuable in estimating the relative importance of factors affecting the movement of petroleum in the shallow subsurface. In addition to two-dimensional simulations, one-dimensional simulations can be used to examine the effects of water-table fluctuations in more detail and to analyze laboratory column experiments.

In certain situations, the boundary between petroleum-saturated and water-saturated regions may be relatively sharp with a very narrow transition zone in which both water and petroleum are mobile. In such cases, it may be possible to develop "sharp-interface" models in which regions of single-phase petroleum flow and single-phase water flow are separated by a sharp boundary that is free to move with time. Models of this type have been used in the petroleum industry to describe the flow of petroleum and water in "gravity segregated" reservoirs characterized by petroleum-saturated zones overlying water-saturated zones (Aziz and Settari, 1979, p. 376-383). In general, interface models fall into two basic categories: (1) areal-flow models in which the position of the interface is computed implicitly as a function of potentials in the respective fluids, and (2) vertical cross-sectional models in which the interface between the two fluids is explicitly represented and treated as a moving boundary in transient-flow systems. For large-scale problems, the reduction in computational effort afforded by sharp-interface models, compared with traditional multiphase-flow models, may allow simulation of moving petroleum layers that otherwise would be impractical to simulate. At present, it is not known which situations, if any, may be amenable to the sharp-interface approximation. However, by simulating a variety of hypothetical systems using traditional multiphase-flow models it should be possible to evaluate the potential of sharp-interface models for the analysis of petroleum spills. This area of research deserves further investigation.

The extent to which models describing the movement of petroleum in the subsurface can be applied and tested at the Bemidji site depends on the ability of surface and borehole geophysical techniques to define the petroleum lens and measure petroleum saturation. If geophysical techniques do not prove useful in defining the petroleum layer and only information from wells and cores is available, study of the movement of the petroleum phase will be severely limited. However, assuming that satisfactory nonintrusive measurement techniques can be developed, the Bemidji site provides an excellent opportunity

to study the long-term movement of a floating petroleum phase. In particular, it should be possible to study in detail the vertical movement of the petroleum lens as it responds to water-table fluctuations. In addition, multiphase flow simulations based on conditions at the Bemidji site may provide first-order estimates of the large-scale movement of the petroleum layer that can be compared with field measurements to improve the conceptual model of petroleum-phase flow.

### Transport in the Unsaturated Zone

Presently, transport of petroleum constituents in the unsaturated zone at the Bemidji site is primarily due to: (1) diffusion of volatiles in the gas phase, and (2) movement of dissolved components in water. After initial infiltration, petroleum is either absent from the unsaturated zone or present as an immobile residual. If chemical equilibrium exists locally between phases, an analysis of unsaturated water flow and chemical transport requires the solution of one transport equation for each chemical component. If the phases are not in chemical equilibrium locally, a transport equation for each component in each of the phases is required. In either case, the mathematical formulation results in a system of partial differential equations that can be solved numerically. Most of the transport processes in the unsaturated zone can be approximated as one-dimensional in the vertical direction. With one-dimensional models it should be possible to examine such things as (1) the effects of volatile loss on the change in chemical composition of the petroleum, (2) the rate of volatile loss to the atmosphere, and (3) the rate and amount of dissolution of organic constituents during recharge events.

### Transport in the Saturated Zone

Numerical models of solute transport in saturated ground-water systems have been in development for several years and are now well established. The principal contribution from this study will be in the area of improving the mathematical representation of source-sink terms related to petroleum dissolution, biological alteration, and volatile loss to the unsaturated zone. Specifically, at the Bemidji site, measurements of the concentrations of dissolved petroleum components with depth will be made in the vicinity of the water table and the petroleum-water interface. Data on concentration, together with detailed, small-scale solute-transport modeling, will yield useful information on the rate of dissolution at the petroleum-water interface and the rate of volatile loss to the unsaturated zone.

### SUMMARY

Mathematical modeling, in the form of computer simulation, will be helpful in developing an improved understanding of the movement of spilled petroleum. In the shallow subsurface, petroleum and its constitutive compounds move by a complex combination of fluid flow, gas diffusion, and advective and dispersive transport in ground water. From a practical point of view, the best approach to simulating such a complex system may be to separate the problem into a number of smaller, more manageable pieces. The approach outlined in this report is to analyze the problem in three parts: (1) multiphase fluid flow, (2) transport of volatile and dissolved components in the unsaturated zone, and

(3) transport of dissolved petroleum constituents in the saturated zone. By separating the problem into these three parts, it will be possible to examine many of the transport processes in much more detail than would be possible with a comprehensive multiphase-flow, multicomponent chemical-transport model.

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## CHAPTER C

### **MASS-EXCHANGE PROCESSES AT THE PETROLEUM-WATER INTERFACE**

By Hans-Olaf Pfannkuch<sup>1</sup>

#### **ABSTRACT**

After a petroleum spill, the oil-infiltration body constitutes the source of dissolved substances in the shallow ground-water-flow system. Its extent and volume, physico-chemical and hydrodynamic properties determine its strength and persistence as a source.

Compound solubilities, rate constants and the hydrodynamic-flow regime establish the rate-determining step in the reaction sequence between oil and water. The actual area of oil-water contact is the interface across which mass exchange occurs. It governs the actual mass that is exchanged in a given period. Due to the complex morphology of the pore space and resulting saturation-dependent, capillary phenomena, the quantification of this area is exceedingly difficult. The use of capillary pressure functions to determine internal interface areas is suggested.

Experimentally derived values of exchange coefficients for various flow velocities in porous media were recast in dimensionless form. The dimensionless mass exchange expressed as a Sherwood number depends on the flow regime expressed as a Peclet number. It is concluded that for most ground-water-flow situations, mass exchange is diffusion controlled and independent of flow rates.

The source strength ( $m_s$ ) is the total dissolved mass of petroleum substance released into the ground-water system over the existence ( $t_c$ ) of the infiltration-oil body:

$$m_s = k(\text{grad } C, Pe, Re, Sc, D, G \dots) \cdot A(S_i, P_c, \frac{dA}{dt}) \cdot t_c$$

Appropriate source characterization is an integral part of formulating predictive flow and mass transport models and it is important in the assessment and design of source-control schemes for pollution abatement procedures.

#### **INTRODUCTION**

The release of hydrophobic organic fluids, such as petroleum, into the subsurface and shallow ground-water system produces a characteristic

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distribution of the oil phase. Where this oil phase is in contact with water, it is a source for dissolved constituents that can move with ground water. Dissolved hydrocarbons at low concentrations can contaminate large volumes of the ground-water system in a relatively short time. Oil in the free phase moves much more slowly due to lower effective permeabilities in multiphase flow regions. It tends to be immobilized and contained in a relatively small volume of the aquifer due to capillary forces. Nevertheless, the ultimate distribution and shape of the oil body, and interface with the water determines and controls the source strength for the dissolved components. The purpose of this paper is to provide a general overview of the physical basis for exchange processes between the petroleum source, water, and gas in the shallow subsurface.

## INFILTRATION AND MASS EXCHANGE IN SHALLOW AQUIFERS

### Structure of the Oil-Infiltration Body

The structure of the infiltration body and the hydrodynamic and capillary flow regimes characteristic of it determine the form and nature of the oil-water interfaces and the dominant reaction mechanisms and, thereby, materially influence the type of exchange processes (Schwille, 1966).

After a spill at or near the land surface, the oil-infiltration body is propagated into the subsurface in successive time steps and along different migration paths (Convery, 1979; Pfannkuch and others, 1979; Eames, 1981; Pfannkuch, 1982). Six functional zones can be identified in the vicinity of an oil spill and are shown in figure 7. For each zone, characteristic settings for the mass transfer process can be identified. These will be discussed later, but the different sites, A to H, are also given on figure 7.

Surface Zone (I).--The initial surface accumulation of hydrocarbons is controlled substantially by the topography of the spill site. Topography determines the initial areal extent of the ponding area from which infiltration into the subsurface takes place, and, thereby, influences the shape and extent of the oil-infiltration body.

Soil Zone (II).--Organic soils, where present, influence oil-retention capacity. Because organic soils usually are oil wet or liophillic under a spill, oil saturation may be higher in the soil zone than in lower zones.

Vadose Zone (III).--This is the originally partially water-saturated region between the bottom of the soil zone and the water table. Oil movement is mostly vertically downward, but some lateral spreading also occurs because of capillary forces. The actual retention of the oil is a complex function of the capillary character of this zone, the oil-water air saturation, and saturation history. The ultimate oil-retention capacity of this zone determines how much oil will actually be in contact with flowing ground water.

Capillary Contact Zone (IV).--Oil that cannot be retained in zone III reaches the capillary fringe and spreads laterally through it. The oil forms a lens-shaped body on the water table. The extent and shape of this lens is a function of the capillary forces in the capillary fringe, the head in the free

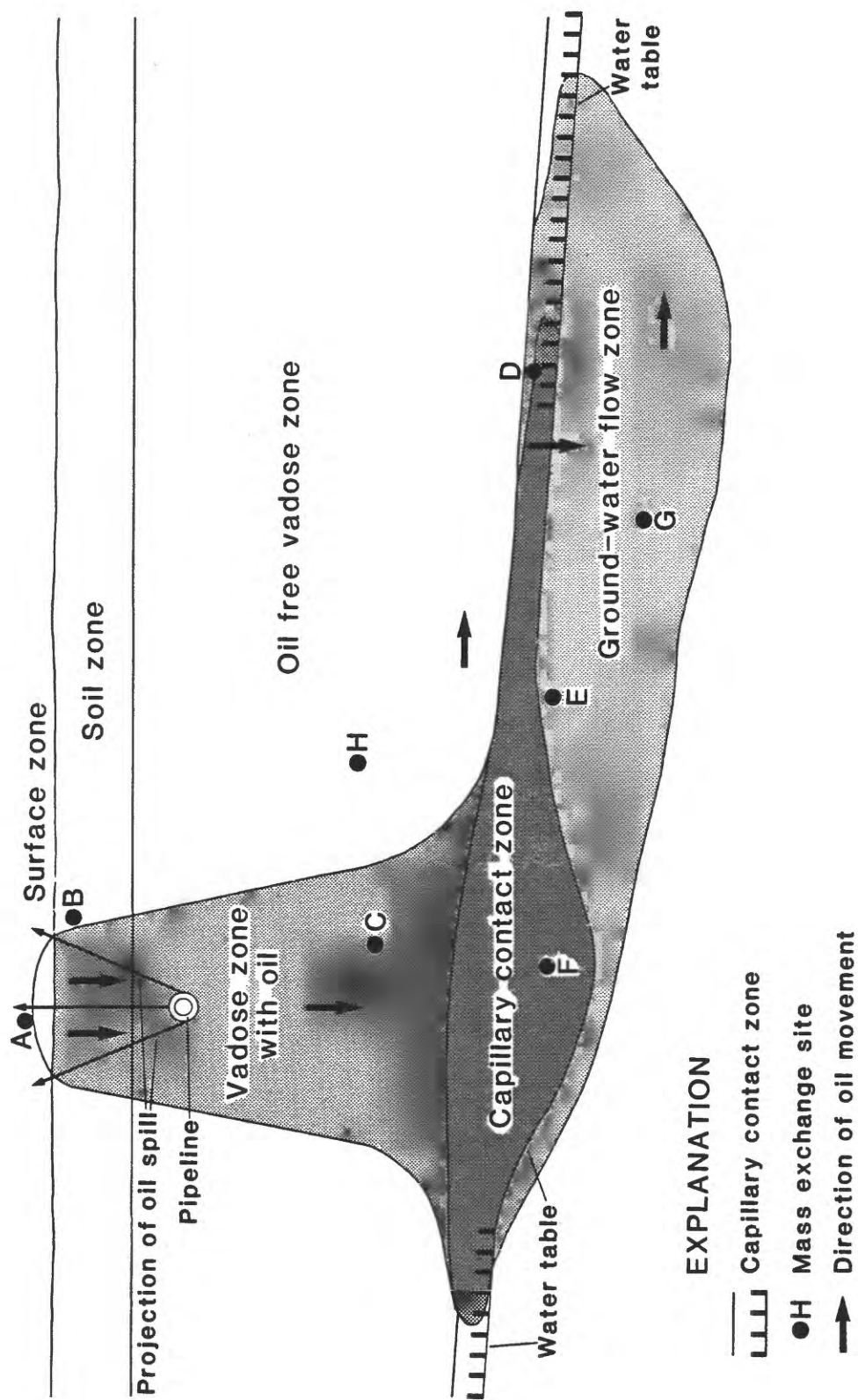


Figure 7.--Vertical structure of oil-infiltration body and location of mass-exchange sites.

oil phase, and the slope of the water table. It is across this interface that the first mass exchange between the oil body and flowing ground water takes place. An initially sharp oil-water contact may be disintegrated through water-table fluctuations. This periodic vertical displacement results in trapping of oil globules in capillary spaces and hence in an increase of the contact area for effective mass exchange.

Ground-Water Flow Zone (V).--Flow in the saturated zone is predominantly horizontal. Dissolved hydrocarbon constituents are rapidly carried away by advective-dispersive transport mechanisms. In this zone, hydrocarbon contamination has the highest mobility and the greatest potential to affect large volumes of the aquifer.

Oil-Free Vadose Zone (VI).--Volatile components of the oil will evaporate from Zones II and III and form a gaseous envelope around the infiltration body in the otherwise oil-free vadose zone. These vapors may migrate and recondense in other locations. Analysis of the soil atmosphere, where positive, can be used as a simple tool to determine the extent of shallow oil lenses.

### Source Strength--General Definition

The intensity with which dissolved hydrocarbon constituents are released from the oil-infiltration body can be expressed as source strength,  $m_s$ , which is the total mass released over time. Dimensions are  $[M/T]$ .

The total mass that is transferred from the different zones of an infiltration body as a dissolved constituent into the flowing ground-water zone over time can be used to define the total strength of the source. This is an important factor in the assessment of the total pollution potential and the persistence of the source. It will depend on four sets of factors:

1. Physico-chemical factors as determined by the properties of the hydrocarbon, water, and gas phases.
2. Hydrodynamic factors and flow regime.
3. Hydrologic characteristics of the matrix and saturation distribution.
4. Environmental factors that influence solubilities and rate constants.

In bulk movement, the hydrocarbon and water phases can be considered as two distinct immiscible phases. Solubilities in water are low and range from fractions of a parts per million to several thousand parts per million for aromatics (McAuliffe, 1966; Price, 1976). The presence of the solute in most cases is insufficient to alter hydrologic characteristics and other bulk parameters of the solvent or ground-water phase. However, from a contamination point of view even small dissolved quantities can render a water supply unusable for reasons of taste or health risks. It is, therefore, important to characterize the source, the mass-transfer conditions and its persistence in time.

### Source Strength—Experimental Determination

Only a few experimental studies have defined the source strength of an oil-infiltration body and the dominant mechanisms and process parameters. The two sources used in this review differ in their conclusions about velocity dependence of the process.

#### Mass-Exchange Coefficients at Surface Contacts

The first set of experiments was done by Hoffmann (1969, 1970). He defines the strength of the sources (S) as the amount of dissolved substances transferred into the ground water per unit time ( $k_m$ ) from the infiltration-oil body per unit contact area (A):

$$S = k_m A \quad (1)$$

The experiments were run with a stagnant oil phase retained in the upper half of a porous medium with water flowing at different pore velocities along the contact. Hoffmann's results for a domestic fuel oil-water system yielded mass-exchange coefficients about one to two orders of magnitude smaller than rough estimates for the mass-exchange coefficients given by Working Group (1970) in the table below. The Working Group considered the exchange coefficient as constant with time and independent of ground-water-flow velocities.

Hydrocarbon	Mass-exchange coefficients <sup>1</sup> , $k_m$ [mg/m <sup>2</sup> /s]
Gasoline, tar oil	0.1
Fuel oil, diesel, kerosene	0.01
Lub oils, heavy fuel oil	0.001

<sup>1</sup> Working Group (1970)

A set of similar experiments, but over a wider range of experimental conditions and with tighter control, was carried out in the French national science center's (CNRS) fluid mechanics laboratories at the University of Strasbourg. The results are summarized in Zilliox and others (1973, 1974) and Fried and others (1979). The first set of experiments concentrated on the study of the exchange coefficient,  $k_m$ , as defined in equation 1, and its dependence on flow velocities. Preliminary experiments established the exchange coefficients between stagnant gas-oil and a Kuwait crude, respectively, and flowing water across a free contact surface. The experiments showed a strong dependence of  $k_m$  on the flow velocity of the water. Experiments in a porous medium were conducted with gas-oil only. The interface area used for the calculations was the externally measured areal extent of the oil-water contact. Values for  $k_m$  range from 100 to 1,000 x 10<sup>-6</sup> mg/m<sup>2</sup>s<sup>-1</sup> and show a marked dependence on ground-water-flow velocities. Zilliox's experiments also indicate a decline of the exchange coefficient with time as the oil

ages. Fluctuations of the water table rejuvenate the dissolution process and increase  $k_m$  if oil is trapped below the water table. The results of experiments by Hoffman and Zilliox are summarized in table 3.

### **Mass-Exchange Coefficient at Volumetrically Defined Contacts**

For cases where residual oil is trapped in the saturated zone in globule or ganglion form, it is not possible to determine the oil-water contact area easily. To describe mass exchange in such cases, a volumetric-exchange coefficient  $k_{mv}$  was defined by Zilliox and others (1973) as,

$$k_{mv} = \frac{(\dot{m}/dt)}{V} \quad (2)$$

A similar strong velocity dependence and an aging effect on  $k_{mv}$  can be shown as on  $k_m$ .

Subsequent experiments by Zilliox and others (1978) have shown that the mass-exchange rate in a water-saturated medium with residual oil is extremely effective and that a contact time of only about 15 minutes is necessary to reach equilibrium saturation values. This has been confirmed for unsaturated column experiments by Van der Waarden and others (1971) and for saturated conditions by Bastien and others (1975).

### **Discussion of Literature Review**

Literature research indicates that there are unresolved questions whether and how the mass-exchange coefficient depends on the dissolution rates and the flow velocities of the carrier. The source strength is a function of the interfacial contact area. Literature values for  $k_m$  vary over a wide range (table 3), probably due to differences in (1) oil composition and (2) geometry of the experimental configuration such as oil volume, contact areas, pore structure, experimental conditions, sampling, sample conservation, and measurement techniques. When equilibrium conditions can be postulated, the resulting reaction and exchange relations take the form of exponential equations.

The transfer processes are first studied from a simple thermodynamic and physical-chemistry point of view for ideal configurations of multiphase fluid interfaces. The findings then can be transferred to the more complex aquifer case to elucidate the question of the flow-velocity dependence.

### **INTERPHASE MASS EXCHANGE**

The main thrust of the theoretical and experimental development in the chemical engineering literature has been in the area of gas-liquid and solid-liquid exchange reactions in multiphase systems. Relatively little direct attention has been given to two-phase liquid-liquid reactions. Much of the theory, however, can be directly transferred to this particular application.

**Table 3.—Hydrocarbon-ground water mass-exchange coefficients: experimental results (from Zilliox and others, 1973)**

[For all experiments, D equals  $2.0 \times 10^{-9} \text{ m}^2/\text{s}$ ]

(a) $k_m$ based on apparent contact surface					
$u$	$k_m$	$d_p$	Pe	Sh	
$[(\text{m/s}) \times 10^{-6}]$	$[(\text{mg}/\text{m}^2\text{s}) \times 10^{-6}]$	$[\text{m} \times 10^{-3}]$			
Zilliox and others (1973)					
37.5	666.67	2.0	37.5	66.5	
76.39	944.44	2.0	76.39	94.5	
94.44	916.67	2.0	94.44	91.5	
38.88	263.89	2.0	38.88	26.4	
12.5	83.33	2.0	12.5	8.35	
36.11	277.78	2.0	36.11	27.80	
51.39	1,027.78	2.0	51.39	103.00	
48.61	611.11	2.0	48.61	61.00	
Hoffmann (1969)					
2.6	16.66	.5	.65	.42	
6.66	27.77	.5	1.67	.70	
13.33	19.44	.5	3.33	.49	
21.66	25.00	.5	5.42	.63	
50.00	41.66	.5	12.5	1.08	
66.67	77.77	.5	16.67	1.95	
108.33	13.88	.5	27.08	0.35	
166.67	305.55	.5	41.67	7.65	
(b) $k_{mv}$ based on volume source					
$u$	$k_{mv}$	$d_p$	Pe	Sh	
$[(\text{m/s}) \times 10^{-6}]$	$[(\text{mg}/\text{m}^3\text{s}) \times 10^{-6}]$	$[\text{m} \times 10^{-3}]$			
Zilliox and others (1973)					
302.8	115.3	2.0	302.8	367.	
179.2 <sup>a</sup>	61.4 <sup>a</sup>	2.0 <sup>a</sup>	179.2 <sup>a</sup>	195.4 <sup>a</sup>	
70.8	25.3	2.0	70.8	80.5	
226.4	75.6	2.0	226.4	240.5	
270.8	82.2	2.0	270.8	261.7	
422.2	94.7	2.0	422.2	301.5	
847.2	168.9	2.0	847.2	537.5	
1,131.9	206.1	2.0	1,131.9	655.9	

<sup>a</sup> Used in figure 12.

### Conceptual Models and Definitions

From a phenomenological point of view, mass exchange at an interface consists of two basic reactions—the dissolution reaction at the surface and diffusion and (or) hydrodynamic transport away from it.

The basic characteristic of an oil-water interface is the extremely low solubility of the two phases into each other. In most cases of practical interest, the oil phase is constituted of many hydrocarbon components with varying boiling points, mole volumes, and other physico-chemical characteristics that make the description of exchange processes more complex than for a homogeneous composition. Because the interface is not rigid, it will deform under hydrodynamic stress and will change location in response to dissolution, which makes analytical treatment difficult.

For the present discussion we shall consider only mass-exchange from oil into water, although solution of water into oil also can take place. At least two if not more consecutive transfer processes take place and it becomes important, therefore, to determine which processes, if any, are rate-limiting. The principal steps are (1) the dissolution reaction at the interface, (2) the diffusive transport of dissolved products away from the interface into the water, (3) transport of the solute from the interior of the globule to the interface in multicomponent oils, and (4) advective transport of water to the oil surface.

For the present, it is assumed that only true solution takes place, although hydrocarbons also may move in the form of micelles. If the oil phase has a range of intermixed components of varying individual solubilities, selective leaching will take place where the more volatile components will dissolve first, leaving behind a less and less soluble residue.

For a simple component, the following equations can be written for the reaction rate per unit interfacial area  $1/A(dm/dt)_r$  and the diffusion rate  $1/A(dm/dt)_d$ :

$$\frac{1}{A} \left[ \frac{dm}{dt} \right]_r = r C_i \quad (3)$$

and

$$\frac{1}{A} \left[ \frac{dm}{dt} \right]_d = \frac{D}{n} (C_f - C_i) \quad (4)$$

If the reaction is described by first order kinetics, as most solution reactions are, continuity requires the two rates to be the same at the interface, and the following holds:

$$\frac{1}{A} \left[ \frac{dm}{dt} \right]_r = \frac{1}{A} \left[ \frac{dm}{dt} \right]_d = \frac{r (D/n) C_f}{r + (D/n)} \quad (5)$$

If  $(D/n) \gg r$  the reaction is solubility controlled, if  $(D/n) \ll r$  the reaction is diffusion controlled.

In multicomponent hydrocarbon systems, the rate limiting step may shift from initially solubility controlled to diffusion controlled in later stages.

The ratio  $D/n$  takes on the meaning of an exchange coefficient. But under practical situations it is easier to define it in terms of mass exchange per unit area and unit time,  $k_m$ , where mass may be given in moles or milligrams. The coefficient also can be defined as above and referred to the molar volume ( $L^3/M$ ) of the solute, in which case the dimensions become  $k(L/T)$  which gives it the sense of a permeability coefficient.

### Film- and Penetration-Theory Models

Two basic models for mass exchange at boundaries have been proposed. They are the "film theory" and the "penetration theory" (Azbel, 1981).

The film model implies that the mass exchange rate is controlled by the rate of molecular diffusion through a nearly stagnant film at the surface. From equation 4, the mass-exchange coefficient ( $k$ ) takes the form

$$k = \frac{D}{n_{\text{eff}}} \quad (6)$$

where  $n_{\text{eff}}$  is the equivalent boundary layer thickness in which the molecular diffusion has the same effective flux resistance as if it were defined by convective diffusion.

Extension of the film theory to boundary-layer theory considers the effect of advective and convective fluid motion from which a velocity profile normal to the surface can be established. For solid-liquid flows and simple geometries this profile is straightforward. For liquid-liquid interfaces, the analytical description and form of the profile becomes more problematic.

For the hypothetical case of flow along a flat plate with constant surface concentration into a fluid with a linear and constant velocity profile, the mass-exchange equation can be solved and either the local or averaged mass exchange coefficients are found to vary with  $D^{2/3}$ .

The rate of exchange, therefore, depends on the  $2/3$  power of the diffusivity, not the first power as the simpler, stagnant-film theory from equation 6 would suggest.

The penetration theory views mass exchange as an unsteady time-dependent process in which exchange takes place during brief repeated contacts of the solvent with the interface. The advection of fresh solvent to the surface is effected by eddy turbulence in the bulk fluid. Solute is transported away from the interface, leaving a fresh surface from which the process can continue.

For an infinite slab (of fluid) and uniform and constant concentration at the surface, solving equation 6 for the exchange coefficient  $k$  shows it to be dependent in  $D^{1/2}$ , again different from the two definitions above.

### Dimensional Analysis and Semi-Empirical Approach

As the complexities of the interfacial geometry, flow conditions, and transfer mechanisms increase, analytical solutions become untractable. One has to use empirical or semi-empirical approaches by way of the Buckingham Pi theorem, similarity theory and dimensionless groups in order to approximately describe the transfer coefficient.

A dimensionless form of the mass exchange coefficient is the Sherwood number (Sh) which is defined as:

$$Sh = \frac{k d_c}{D} \quad (7)$$

where  $d_c$  is a characteristic length of the system. Based on dimensional analysis, the dimensionless exchange coefficient will depend on flow velocities, momentum, diffusional transport, inertia, and capillary effects, as well as the geometry of the flow region.

At this point it is necessary to summarize the various definitions of mass-exchange coefficients and their relation to the contact areas from which they have been defined. Inspection of the simple definition equation for the local mass-exchange coefficient shows its dimensions as:

$$k \text{ (del C)} = \frac{\delta^2 m}{\delta t \delta A}; \text{ hence } : k = \left[ \frac{M}{TL^2} \right] \left[ \frac{L^3}{M} \right] = \left[ \frac{L}{T} \right] \quad (8)$$

Insertion of this coefficient into the Sherwood group leads to nondimensionality. However, as is often the case, the exchange coefficient in porous media is defined as the mass exchanged (in moles or mg) per unit time and unit area

$$k_m \left[ \frac{M}{L^2 T} \right]$$

In order to convert this expression back into the proper dimensional form, it is multiplied by the mole volume of the substance, V/mole or V/mg. If this information is not available, the Sherwood number is found by

$$Sh = \frac{k_m \cdot d_c}{(\text{del C}) D} \quad (9)$$

In the absence of actually measured concentrations in the pore or reaction space, and if the effluent concentrations are known,  $\text{del C}$  can be taken as the difference between effluent concentration and equilibrium or saturated concentration.

Because it also is difficult to estimate the exact interfacial contact area, sometimes it is necessary to define exchange coefficients ( $k_{ms}$ ) based on

a per unit effective surface area using the externally observable interface, ( $A_p$ ) or ( $k_{mv}$ ), based on the surface displayed per unit volume of a two phase mixture. These coefficients are related in the following way

$$k_m A = k_{ms} A_p = k_{mv} \cdot V \quad (10)$$

In the phenomenological approach, all information concerning the kinetics of the process and the contact surfaces is concentrated and lumped into the empirical coefficients. This means that the mass exchange interface ( $A$ ) on which the definition of the coefficient is based becomes a separate factor of investigation.

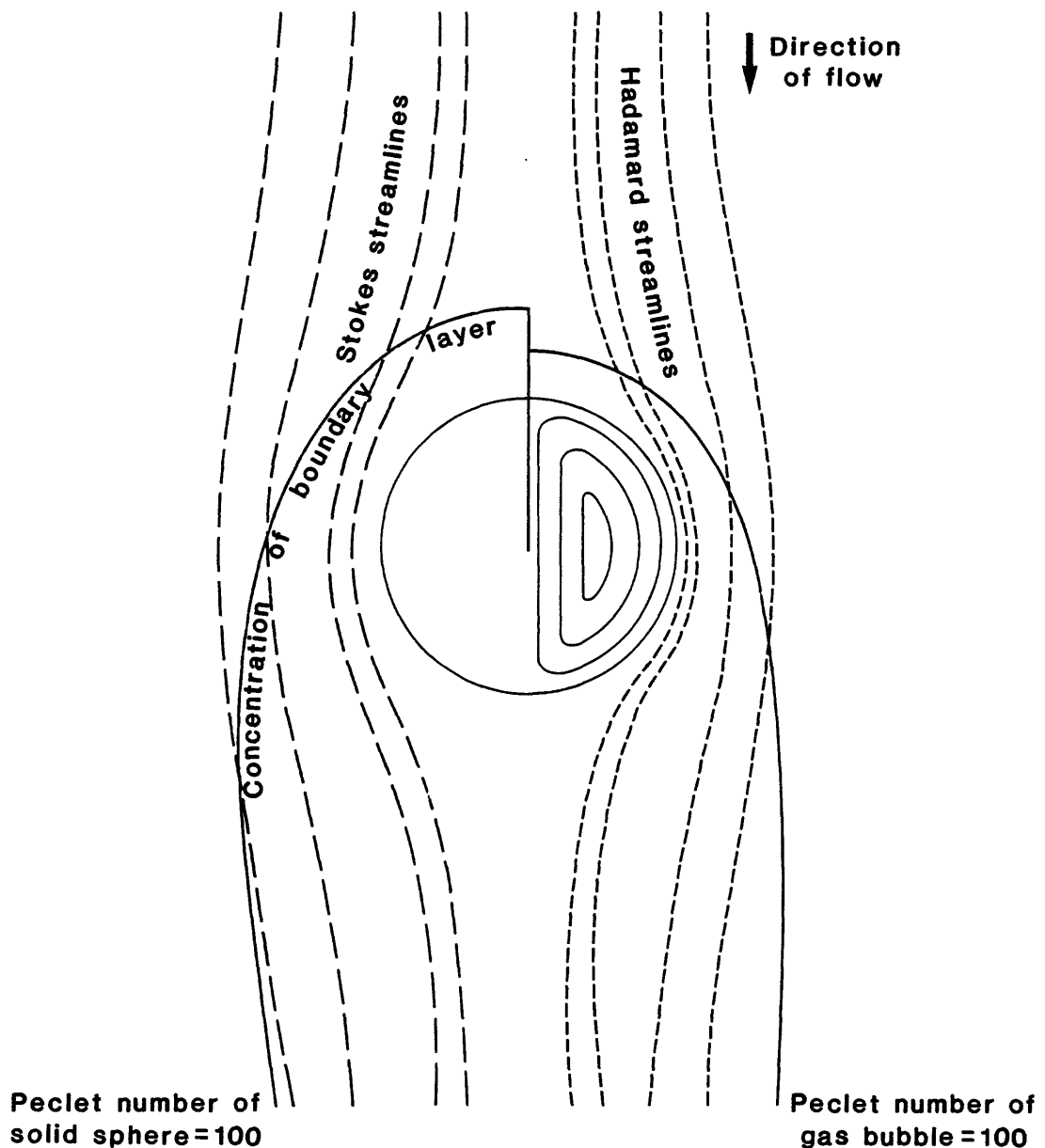
### MASS EXCHANGE IN COMPLEX MEDIA

Transfer processes in ideal systems without the influence of external boundaries are studied first. Then the results are transferred to aquifer media characterized by the irregular-morphology and confined-volume restrictions of small pore spaces.

#### Spheres in Infinite Media

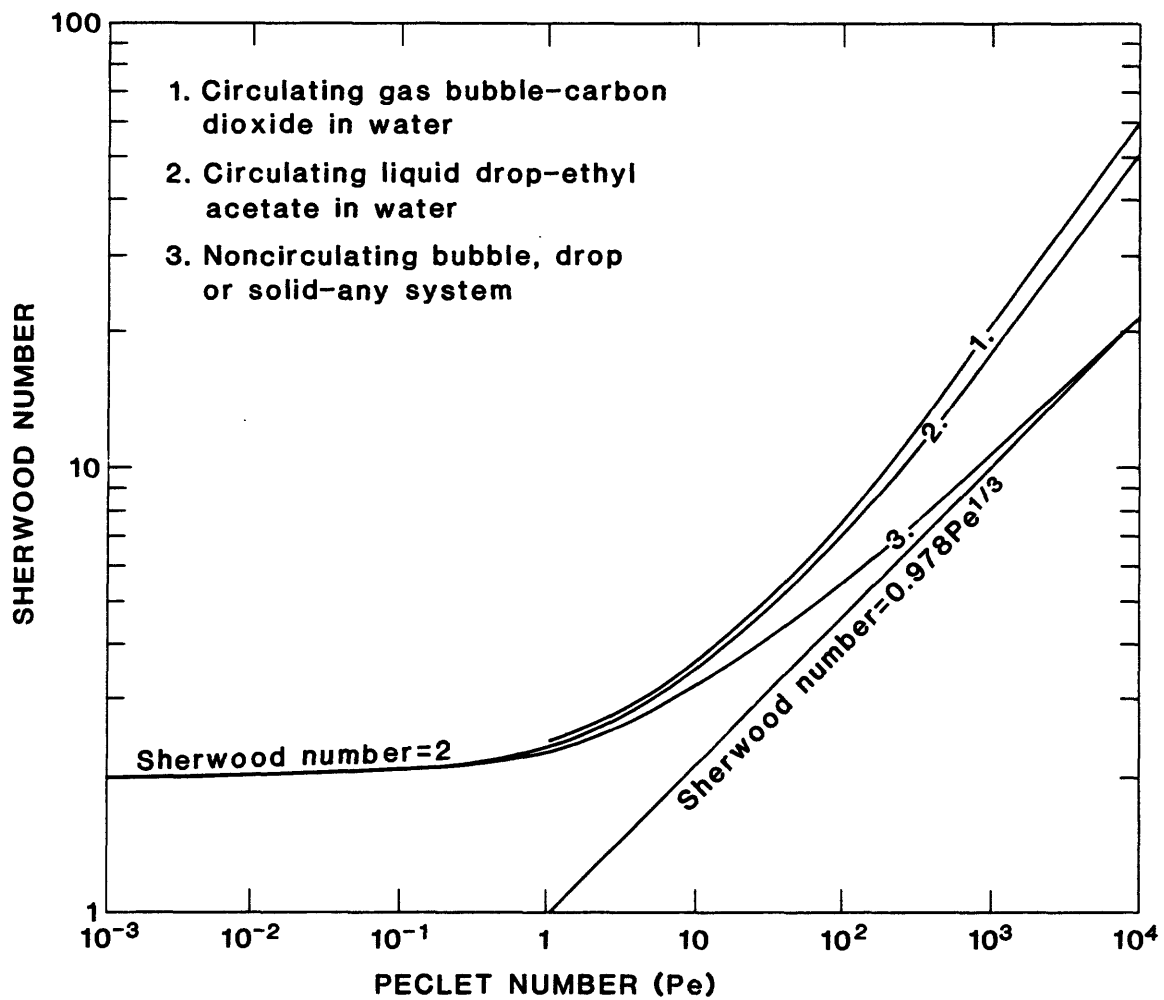
Consider mass exchange from or to a solid or fluid sphere in an infinite medium as a first approximation. Using a single sphere as a starting point is not totally unrealistic as flow around single spheres and assemblages of spheres has been used to develop the drag theory for permeability of porous media. A study by Bowman and others (1961) of mass exchange from fluid and solid spheres in a laminar flow regime considered steady-state diffusion from a fixed spherical particle of a given radius to a continuous fluid medium flowing past the sphere at low Reynolds numbers. Without going into the mathematical development (Bowman and others, 1961), the method consists of solving the stream function around the sphere to define the flow field in the steady state. Specifically, the velocity layer or local profile on the spherical surface is determined among other things as a function of angular position in the spherical coordinates. The diffusion process establishes a mass or concentration boundary layer, and convective-diffusive mass exchange follows.

The flow field as represented by streamlines and the resulting concentration envelope is shown in figure 8, where the left half is the solution for a solid sphere. The right half is for a fluid sphere, in this case gas, with internal circulation as indicated by the inside flow lines. As can be gathered intuitively, internal circulation gives rise to a thinner or smaller boundary layer ( $n_{eff}$ ) and, therefore, leads to a higher exchange coefficient.



**Figure 8.--Comparison of solid and fluid sphere in forced convection.**

If the calculated values of the Sherwood number are plotted against the dimensionless velocity given by the Peclet number  $Pe = u \cdot d/D$ , the resulting curve has four segments (fig. 9). It shows that the exchange coefficient is independent of velocity ( $u$ ) below a critical Peclet number,  $Pe < 1.0$ , that it varies with velocity and Peclet number to the power of 0.33 for solid particles and noncirculating fluid spheres for  $Pe > 100$ . Circulating spheres have higher mass exchange coefficients as indicated by the upper segment of the branched



**Figure 9.--Mass transfer from fluid and solid spheres .**

curve at  $Pe > 1$ . Internal circulation helps bring new solute to the exchange surface from within, and the greater flow velocities (closer streamlines) in the external flow field assure a more efficient convective removal of solute from the boundary layer.

For thin boundary layers (i.e., high  $Pe$ ) and for solid spheres, one form of the solution (as indicated on figure 9) is

$$Sh = b(Pe)^{1/3} \quad (11)$$

where  $b$  is a constant depending on the particular flow profile used. For thick boundary layers (small  $Pe$ ) and both for solid and fluid spheres the expression is a polynomial expansion of the form

$$Sh = 2 + b_1 Pe + b_2 Pe^2 + b_3 Pe^3 + \dots \quad (12)$$

with the  $b_i$ 's again constants depending on the flow profiles used. The relations for higher Peclet numbers and circulating spheres become complex and take the form

$$Sh = f(Re, VIS, DEN) Pe^{1/2} \quad (13)$$

where  $VIS$  is the viscosity and  $DEN$  the density.

Other phenomena that have been observed in idealized experiments with single droplets or spheres are:

- Decrease of exchange coefficient with time due to the formation of a diffusion resistance through buildup of a surface layer of surfactant substances or the growth of a resistant rind by differential leaching of a multicomponent liquid.
- Occurrence of spontaneous interfacial turbulence and spontaneous emulsification due to imbalances of surface active substances on the interface which create surface tension gradients.

### Mass Exchange in Aquifers

Based on the theoretical analysis from the previous section, the most important factors in total mass exchange from an infiltrated oil body to flowing ground water are determined by fluid properties such as solubilities and rate constants, the phase distribution, and the hydrodynamic regime.

## General Considerations for Porous Media

The fluid properties of interest in the porous medium case are the same as for mass exchange in a free and continuous medium. The parameters are the equilibrium concentrations, reaction mechanisms and rate constants, diffusivities in simple two-component and multicomponent systems, the influence of surfactants and the change in composition and permeability of the interface with time, the viscosity ratios of the dispersed and the continuous phases, and interfacial tensions and interfacial and surface energies. As a whole, the influence of the above parameters is expected to remain the same in the porous medium as in the free phase. However, studies are needed to determine if changes can be effected by the porous medium, such as possible changes in solubility over intensely curved capillary interfaces, introduction of surfactants present in the soil profile, such as humic compounds, and differential depletion of the oil phase resulting in a change in composition by selective adsorption to active surfaces.

The porous medium itself provides the pore spaces in which the different phases can interact. For primary and intergranular flow spaces, pore size, as quantified by some characteristic length dimension such as the pore radius or the hydraulic pore radius, is most strongly determined by the grain size, packing and other textural parameters. The internal pore morphology determines the crucial capillary dimensions such as pore entry radius and branching points and the network conduit structure of the porous medium through the arrangement of pore doublets or manifolds. These are the structures in which multiphase fluids can eventually be trapped and immobilized. Pore morphology also provides the total internal mineral surface area over which the wetting phase can spread. The pore size characteristic ( $d_p$ ) and flow path geometries and tortuosities determine the hydraulic conductivity and intrinsic permeability of the system. The total sum of pore spaces determines the total saturated, monophasic holding capacity or pore volume, although the accessibility of the pore spaces and their retention capacity in the multiphase regime depends on the capillary properties of the system, specifically the capillary radius. Two media with the same bulk pore space and porosity may have different capillary retention capacities.

The combination of porous-medium characteristics and fluid properties forms the basis of both static and dynamic capillary phenomena. It determines the actual phase distributions expressed as relative fluid saturations and, thereby, the shape and extent of the interfacial areas across which exchange reactions take place. The relative saturation controls the hydrologic flow regime through the effective permeabilities of multiphase flow. The fluid-solid capillary properties of interest are static and dynamic interfacial tensions and contact angles, which change with time and flow conditions, and change the wetting characteristics of the mineral grain surfaces with respect to the given saturating fluids. The saturation-desaturation history for a given fluid pair is important in the determination of the final phase distribution because of hysteresis effects in the sorption-desorption isotherms. In general, the residual trapped nonwetting phase (oil) will be at greater relative saturation in the desorption case. The differences are especially large

in the transition zone or capillary fringe. A more detailed discussion of capillary flow phenomena in connection with oil spills can be found in van Dam (1967).

### **Contact Area and Capillary-Pressure Function**

The area of the internal exchange interface depends on the degree of dispersion of the different phases. The smaller the pore spaces the smaller the individual trapped oil globules. Therefore, the specific exchange area per unit volume of nonwetting oil phase is greater in a fine grained than in a coarser porous medium for the same saturation. For any given medium, the specific surface area for the nonwetting phase  $A_{snw}$  increases as its saturation decreases, but has to pass through a maximum, because eventually at  $S_{nw} = 0$  the interfacial area becomes zero again. Based on thermodynamic arguments that relate the change in free surface energy to changes in the fluid-fluid interface, Leverett (1941) has related this interfacial contact area to the area under the capillary pressure curve. This form is defective in the limit that suggests that the fluid-fluid interface area becomes very large as the saturation of the wetting phase tends towards zero. Rose (1958) first developed an expression for the internal surface area of a porous medium by applying the Kozeny-Carman capillary model for flow to the thermodynamic free-energy expression for fluid interfaces in porous media (Rose and Bruce, 1949).

### **Mass-Exchange Sites in Infiltration Body**

Earlier discussion and figure 7 have shown the establishment of different zones occupied by the invading oil. The first definition of these zones is based mainly on the hydrodynamics of the emplacement process. Some of the oil phase distribution changes as there is redistribution of the oil body with time and remobilization with percolation of infiltrating precipitation.

For each zone, characteristic settings of the exchange process can be identified, also shown on figure 1 with the location of the different sites. The two discussed in greater detail are the capillary zone-ground water contact and the zone of oil penetration into the zone of water-table fluctuation. For completeness, all sites are briefly enumerated.

Site A, Surface Zone (I). For oil that remains as spray or ponded at the surface, the predominant mass exchange and transformation processes are evaporation of the lighter fractions and weathering of the heavier fractions.

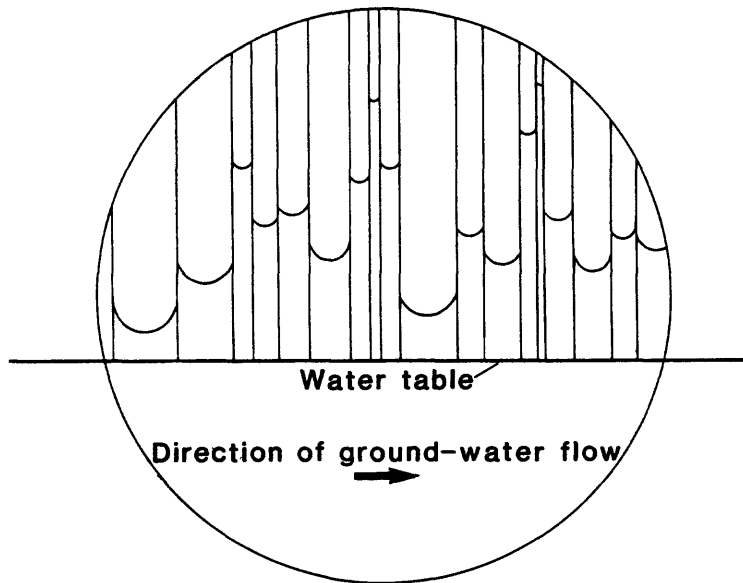
Site B, Soil Zone (II). The soil zone is basically characterized by the same type of distribution and infiltration processes as the subsequent vadose zone, except that the organo-colloidal system also may introduce stronger chromatographic separation effects, different from those in subsequent sites.

Site C, Vadose Zone (III). A three-phase air, gas, oil, and water distribution is established in the pore space. The main characteristic of this site is that during stagnation or relatively slow downward movement the exchange between the oil and the water film in the pendular regime may reach equilibrium conditions. The extent of the interface is a function of the surface properties of the oil, the capillarity of the pore space, and fluid saturation.

Site D, Capillary Zone (IV). After spreading of the continuous oil phase on the water table and through the capillary fringe has stabilized, a lens of finite thickness is formed. In subsequent infiltration and percolation events water droplets pass through the lens and display their surface area to mass exchange.

Site E, Ground-water Contact Zone (IV). As excessive free oil phase reaches the water table it spreads through the capillary fringe. Water saturation ranges from a minute irreducible fraction to practically  $S_w = 1$ . Flow is determined by the effective permeability for the given oil water saturation pair. At rest, a new capillary zone above the water table is created. Capillary rise is influenced by the density difference between the oil and the water. The rise in an idealized capillary ( $h_{cow}$ ) representative of this zone is shown in figure 10 and is given by

$$h_{cow} = \frac{2 (ITEN)_{ow} \cos (TTA)}{(DEN_w - DEN_o) \cdot r} \quad (14)$$



**Figure 10.--Mass exchange at base of capillary fringe.**

The floating oil lens establishes the first contact surface with the flowing ground water at the bottom of the capillary zone. The actual contact area is a complex function of porosity, the areas of the meniscus interfaces, contact angles, and interfacial tensions. In most applied cases, the simple projected area of the oil lens ( $A_o$ ) is equated to the actual contact area with the assumption that the area reduction through porosity is balanced out by lateral contacts in the capillary fringe (Hoffman, 1969). This assumption needs experimental clarification although it seems to be reasonable.

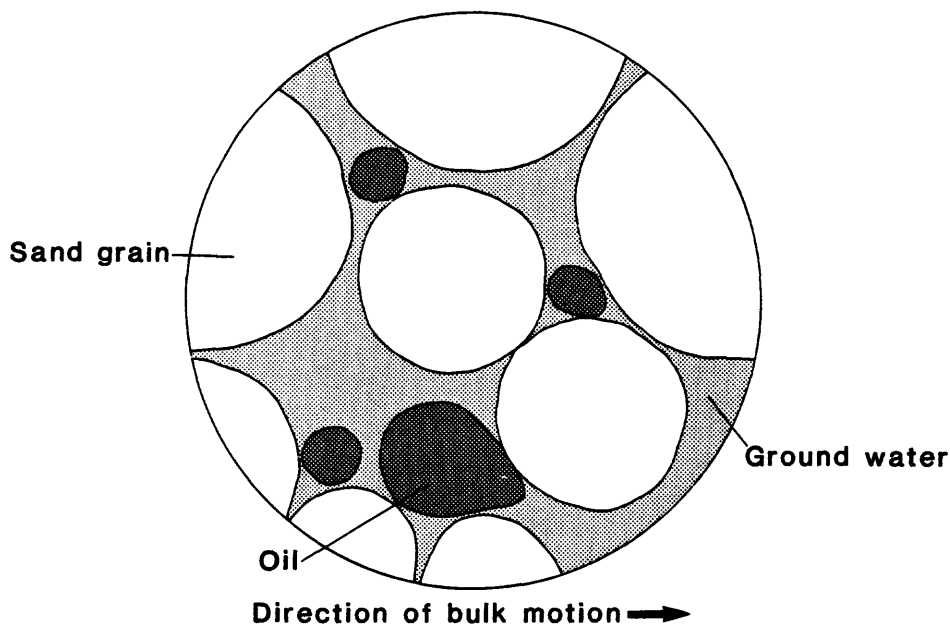
The principal exchange surface is with the flowing ground water, which moves horizontally while the oil in the capillaries remains at rest. For large pores with short capillary rise heights, one can consider a curved interface below which flow occurs and exchange takes place by direct contact and by diffusion into the ground-water stream. For significant capillary rise heights, the oil is first in contact with stagnant capillary water, then with the mobile ground water. For intermediate diameters, a local or internal circulation of capillary water may be initiated, which would enhance the efficiency of the exchange process. For larger  $h_{cow}$  and finer capillary spaces the water will remain stagnant and the exchange process from these interfaces will be controlled by the diffusion process through the capillary tube, rendering the overall process less efficient. When the diffused mass reaches the bottom of the capillary it is carried away by the moving ground water. Capillary diffusion must be added as a second, maybe the principal, rate-limiting step in fine-grained media.

Most experiments by Hoffmann (1970) and Zilliox and others (1978), which will be discussed and evaluated below, were essentially simulating mass exchange at the base of the capillary fringe.

Site F, Ground-water Flow Zone (V). The original column of free oil phase may be sufficiently heavy to depress the water table directly under it. When the oil column is reduced by dissipation into the floating lens, the water table will rise back to near its original position. When the water table fluctuates, some of the oil will be trapped beneath the water table. Residual oil globules will be directly in the ground-water-flow field. The water table fluctuates normally with seasonal recharge or depletion, and also when it is depressed under pumping and allowed to gain its original position after pumping stops (fig. 11).

The approach of Bowman and others (1961) for single droplets is extended to more or less densely packed systems where the proximity of pore walls and increase of interfacial areas might enhance the exchange process. The interfacial area would have to be determined by a more rigorous quantitative application of Rose's (1958) method from capillary pressure functions.

Residual oil saturation usually is small enough that hydraulic conductivity (water) is only marginally affected by reduced effective permeability. Site F also is the zone where, relatively speaking, the largest interfacial areas for mass exchange will be established. This, combined with the higher and continuous ground-water-flow velocities, make this site and site E the most important ones in the exchange of dissolved hydrocarbon constituents to the flowing ground water.



**Figure 11.--Mass exchange from residual oil in zone of water-table fluctuation.**

Site G, Ground-water Flow Zone (V). The greatest mobility of the contaminant as dissolved species is in the zone of saturated flow where diffusion and dispersion add to efficiency of the advective transport. Chromatographic effects can be produced in this zone, and long and short term sorption effects generally occur.

Site H, Oil-free Vadose Zone (VI). The gases filling the pore spaces can be important for mass exchange as in gas absorption reactors by falling films.

#### Dimensional Analysis and Interpretation of Previous Laboratory Experiments

The first part of this paper summarized the only published systematic experimental results of exchange coefficients from gas-oils and fuel oils to ground water. The results are summarized in table 3 on which the data also have been compiled in the form of Peclet and Sherwood numbers.

Grain diameters used as characteristic lengths were inferred from the literature and may not be exact. But, they are uniform for each set of experiments so that interpretation is internally consistent for each one of the experimental conditions ( $d_p = 0.002$  m for Zilliox and  $d_p = 0.0005$  m for Hoffmann). No data for equilibrium concentrations ( $C_s$ ) or solubilities for the oils used was given, nor their exact composition. For both gas-oil and domestic fuel oil, a uniform value for  $C_s = 10^4$  mg/m<sup>3</sup> was chosen. Diffusivity was taken as  $2 \times 10^{-9}$  m<sup>2</sup>/s.

At the time of publication of the results there was considerable discussion whether the mass-exchange coefficients ( $k_m$ ) are flow velocity dependent or not. Hoffmann's experiments seemed to suggest the latter; Zilliox's the former, although with a large scatter. The results also indicated an aging effect, that is, diminishing mass exchange with time, which could easily be due to a decrease of permeability in the surface layer.

By applying Bowman's basic logic and approach, the experimental results were transformed into dimensionless mass exchange coefficients ( $Sh$ ) and flow velocities ( $Pe$ ) and are plotted on figure 12.

The curves have forms basically as predicted by Bowman. The two sets of experiments do not mesh seamlessly, perhaps because the actual grain diameters were different from that mentioned in the literature or because solubilities were different. (A factor of 5 would make the two curves mesh perfectly.) Although there is an offset, the slopes in the velocity dependent portion of the diagram are the same.

The results as presented show that two regimes can be distinguished in mass exchange processes between free hydrocarbon phase and simulated groundwater flow: a velocity independent regime at  $Pe < 1.0$  and  $Sh = 0.55$ . The latter differs from Bowman's value of 2, but this can be explained by the fact that the single sphere in an infinite continuum is free to diffuse whereas the diffusive-controlled exchange mechanism in a porous medium is hindered by the presence of the noncontributing tortuous porous medium. This would reduce the Sherwood number to below 1 when the molecular diffusivity established for a free medium is used in its definition.

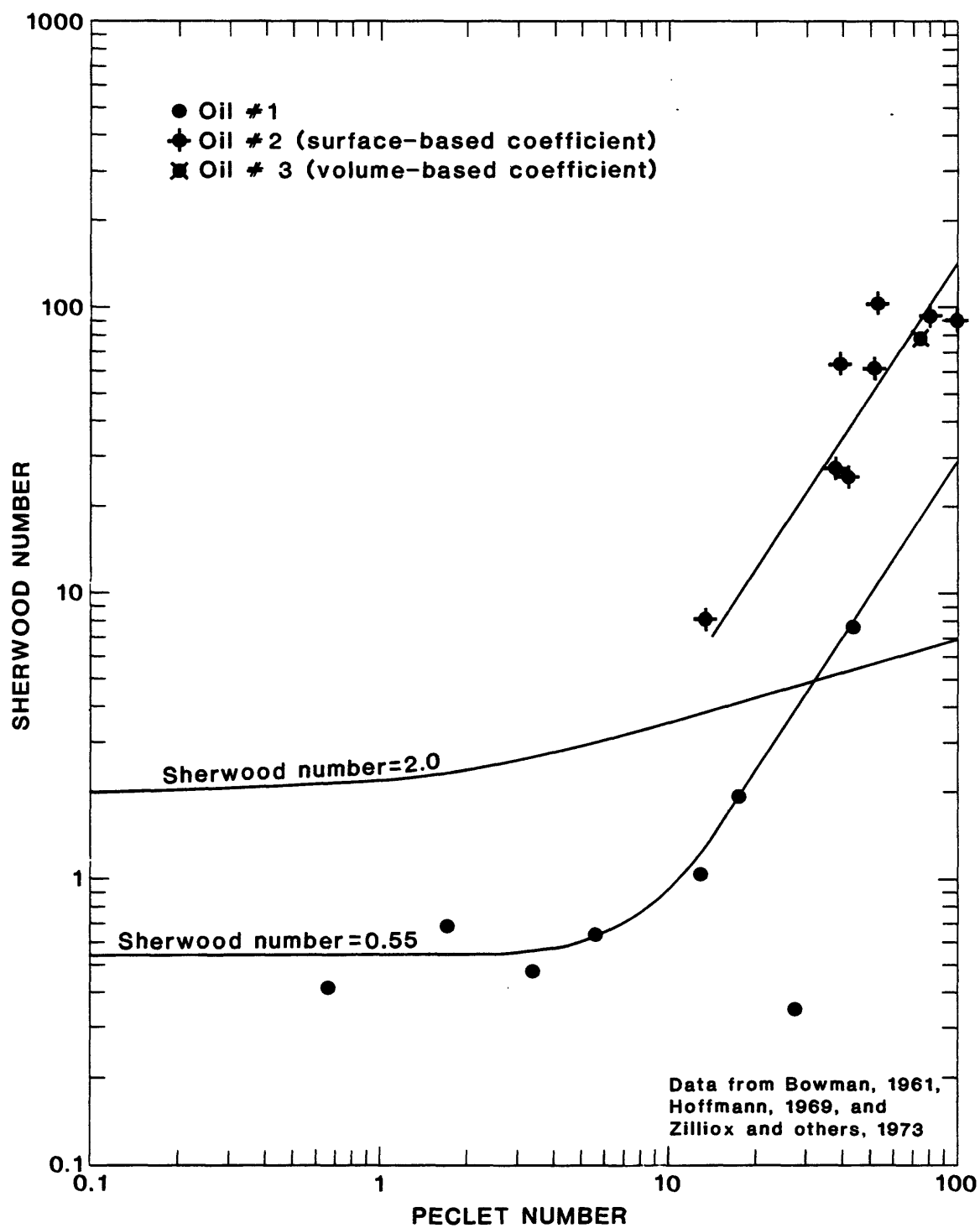
The slopes in the velocity dependent portion of the curves are steeper than those of the Bowman case, which has been plotted for comparison. This could be due to the fact that velocity dependent mass exchange from dispersed surfaces may be enhanced in the porous medium by close juxtaposition of tortuous flow lines and possibly mechanical dispersion and removal or diminishing of the diffuse concentration layer.

The availability of the literature data and supporting information is insufficient to warrant more quantitative statements and analysis. Systematic experiments have to be designed with better control over physico-chemical and porous media flow parameters, where the experimental design can be streamlined according to the appropriate dimensional analysis and formulation of the correct dimensionless groups for which the seminal experiments of Hoffman and Zilliox and their coworkers led the way.

#### SUMMARY AND CONCLUSIONS

Interphase mass exchange between oil and water in aquifer systems is most strongly controlled by:

- The equilibrium solubility of the hydrocarbons in question into the water at the prevailing environmental conditions. The solution kinetics at the interface play a minor role for most substances of interest



**Figure 12.--Oil-to-water mass exchange in porous media.**

because the rate-determining step in the ground-water-flow regime is diffusion.

- The flow regime determines the effectiveness of the exchange through the diffusion layer. At low dimensionless velocities or Peclet numbers, the mass exchange as expressed by a Sherwood number is diffusion controlled and independent of flow velocity. At higher flow velocity, various power laws of dependence on diffusivity and flow velocity hold. Most ground-water flow would be expected to fall into the velocity independent regime at low Peclet numbers.

The contact area between the phases across which exchange occurs provides the opportunity for reaction and, therefore, the absolute amount of mass exchange is directly proportional to it. In a porous medium, the determination of this area is complicated and, therefore, fictitious exchange coefficients have to be defined based on the projected external contact area or on volumes in which residual oil is entrapped and immobilized.

The source strength of an oil infiltration body into the subsurface and shallow aquifer environment can be given as the total mass dissolved ( $m_s$ ) over time of contact ( $t_c$ ). It depends on the mass transfer coefficients and the contact area which, in turn, depend on the parameters in the brackets which have been defined earlier:

$$m_s = k(\text{grad } C, Pe, Re, Sc, D, G \quad \dots) \cdot A(S_i, P_c, \frac{dA}{dt}) \cdot t_c \quad (15)$$

This analysis furnishes the guidelines to design appropriate laboratory experiments under controlled conditions to test the hypothesis developed above. In particular, better control and description of pore morphology, solubility conditions, and range of flow regimes are necessary. For field application, it is necessary to establish whether the mass exchange phenomena are scale dependent, as dispersion apparently is.

In order to get a better idea about actual liquid-liquid exchange areas in a porous medium, its dependence on the capillary pressure function seems to offer a good theoretical approach. The theory has to be worked out in greater detail to be quantitatively applicable and tested by controlled experiments.

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## LIST OF SYMBOLS

A	Interfacial actual contact area between oil and water	[L <sup>2</sup> ]
A <sub>p</sub>	Projected, bulk contact area between oil body and water	[L <sup>2</sup> ]
C	Concentration	[M/L <sup>3</sup> ]
C <sub>s</sub>	Equilibrium solubility	[M/L <sup>3</sup> ]
C <sub>i</sub>	Concentration of solution at water-oil interface	[M/L <sup>3</sup> ]
C <sub>f</sub>	Concentration in bulk fluid	[M/L <sup>3</sup> ]
del C	Concentration difference	[M/L <sup>3</sup> ]
grad C	Concentration gradient	[M/L <sup>4</sup> ]
d	Diameter of sphere, grain	[L]
d <sub>c</sub>	Characteristic length of system	[L]
d <sub>p</sub>	Characteristic length of pore space	[L]
D	Molecular diffusion coefficient	[L <sup>2</sup> /T]
DEN <sub>w</sub> , DEN <sub>o</sub>	Density, water, oil, respectively	[M/L <sup>3</sup> ]
G	Geometric descriptors of flowfield	[0]
h <sub>cow</sub>	Capillary rise—oil-water system	[L]
ITEN	Interfacial tension—oil-water	[M/T <sup>2</sup> ]
k	Transfer coefficient	[L/T]
k <sub>m</sub>	Mass exchange coefficient (based on A)	[M/L <sup>2</sup> T]
k <sub>ms</sub>	Mass exchange coefficient (based on A <sub>p</sub> )	[M/L <sup>2</sup> T]
k <sub>mv</sub>	Mass exchange coefficient (based on V)	[M/L <sup>3</sup> T]
m	Mass	[M]
m <sub>s</sub>	Source strength	[M/T]
(dm/dt) <sub>r</sub>	Reaction rate	[MIT]
(dm/dt) <sub>d</sub>	Diffusion rate	[M/T]

n	Thickness of diffuse boundary layer	[L]
$n_{eff}$	Equivalent boundary layer thickness	[L]
Nu	Nusselt number	[0]
Pe	Peclet number	[0]
r	Reaction constant	[M/T]
Re	Reynolds number	[0]
Sc	Schmidt number	[0]
Sh	Sherwood number	[0]
$S_i$	Saturation (i-th phase)	[0]
t	Time	[T]
TTA	Contact angle—oil-water	[0]
u	Flow velocity	[L/T]
V	Volume	[L <sup>3</sup> ]
VIS	Viscosity	[M/LT]

## CHAPTER D

### **DETERMINATION OF HYDRAULIC CONDUCTIVITY IN THREE DIMENSIONS AND ITS RELATION TO DISPERSIVITY**

By R. T. Miller<sup>1</sup>

#### **ABSTRACT**

Recent investigations suggest that dispersion in aquifers is scale dependent and a function of the heterogeneity of aquifer materials. Theoretical stochastic studies indicate that determining hydraulic-conductivity variability in three dimensions is important in analyzing the dispersion process. Even though field methods are available to approximate hydraulic conductivity in three dimensions, the methods are not generally used because of high cost of field equipment and because measurement and analysis techniques are cumbersome and time consuming.

The hypothesis of this study is that field-determined values of dispersivity are scale dependent and that they may be described as a function of hydraulic conductivity in three dimensions. The objectives of the study at the Bemidji research site are to (1) determine hydraulic conductivity of the porous media in three dimensions, (2) determine field values of dispersivity and its scale dependence on hydraulic conductivity, and (3) develop and apply a computerized data-collection, storage, and analysis system for field use in comprehensive determination of hydraulic conductivity and dispersivity.

Plans for this investigation involve a variety of methods of analysis. Hydraulic conductivity will be determined separately in the horizontal and vertical planes of the hydraulic-conductivity ellipsoid. Field values of dispersivity will be determined by single-well and doublet-well injection or withdrawal tests with tracers. A computerized data-collection, storage, and analysis system to measure pressure, flow rate, tracer concentrations, and temperature will be designed for field testing. Real-time computer programs will be used to analyze field data. The initial methods of analysis will be utilized to meet the objectives of the study.

Preliminary field data indicate the aquifer underlying the Bemidji site is vertically heterogeneous, cross-bedded outwash. Preliminary analysis of the flow field around a hypothetical doublet-well tracer test indicates that the location of the wells can affect the field value of dispersivity. Preliminary analysis also indicates that different values of dispersivity may result from anisotropic conditions in tests in which observation wells are located at equal radial distances from either the injection or withdrawal well.

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## **INTRODUCTION**

Recent investigations by Anderson (1979, 1983), Gelhar and others (1979), Sauty (1980), and Pickens and Grisak (1981) suggest that dispersion in aquifers is scale dependent because, in tracer tests, the greater the travel distance of a tracer, the larger the calculated dispersivity value. Efforts to understand and describe scale dependence of the dispersion process have focused on the effects of heterogeneity of the porous media on hydraulic conductivity. Several theoretical studies have analyzed the effects of heterogeneity through statistical descriptions of spatial variability (Warren and Skiba, 1964; Heller, 1972; Schwartz, 1977; Gelhar and others, 1979; Matheron and DeMarsily, 1980; Smith and Schwartz, 1980; Dagan, 1982). All of these studies demonstrate that heterogeneity enhances the mixing process, and several of them indicate that mixing often can not be described by the classical Fickian model for dispersive transport where mass is diffused in direct proportion to concentration gradients. However, each of these studies assumed simplifications such as perfect stratification, two-dimensional flow, statistical isotropy, or absence of local dispersion. Consequently, the somewhat divergent results of these studies may not represent real complications in the dispersion process. Rather, the results suggest that the various model assumptions may not represent the controlling mechanisms in the field (Gelhar and Axness, 1983).

Gelhar and Axness (1983) use a stochastic analysis to describe dispersion in aquifers in three dimensions. Their theoretical study tested various hypothetical assumptions concerning the anisotropy of hydraulic conductivity in three dimensions. One of their conclusions is that consideration of three-dimensional flow is important in analyzing the dispersion process and that important features are lost when only two-dimensional flow is considered.

In addition, Molz and others (1983) suggest in their examination of the scale-dependence of dispersion that more emphasis is needed on field determination of hydraulic-conductivity variations and other heterogeneities, such as in porosity and velocity distribution, and less emphasis on incorporating somewhat arbitrary dispersion coefficients into complex mathematical models.

While recent investigations have centered on the relation of field-determined values of dispersivity to variations of hydraulic conductivity in the vertical plane, few have considered the relation of dispersivity to variations of hydraulic conductivity in the horizontal plane. Although there are techniques to determine hydraulic conductivity in three dimensions from pumping and injection tests, often these tests are not conducted because of the high cost of installing a sufficient number of measurement points (usually wells), and because manual methods for collecting and interpreting the needed data are cumbersome and time-consuming. Many aquifer tests are unsuccessful because of insufficient test duration, small magnitude of aquifer response, or lack of precision in field measurement. These problems often are not recognized until after the test is completed and data interpreted.

### **Purpose and Scope**

Objectives of this paper are to present the results of a study to test the hypothesis that field-determined values of dispersivity are scale dependent and

may be described as a function of hydraulic conductivity in three dimensions. To test this hypothesis, additional objectives using various methods of analysis are required. They are: (1) determine hydraulic conductivity of the porous media in three dimensions, (2) determine field values of dispersivity and its scale-dependence on hydraulic conductivity, and (3) develop and apply a computerized data-collection, storage, and analysis system for field use in comprehensive determination of hydraulic conductivity and dispersivity.

## METHODS OF STUDY

### Determination of Hydraulic Conductivity

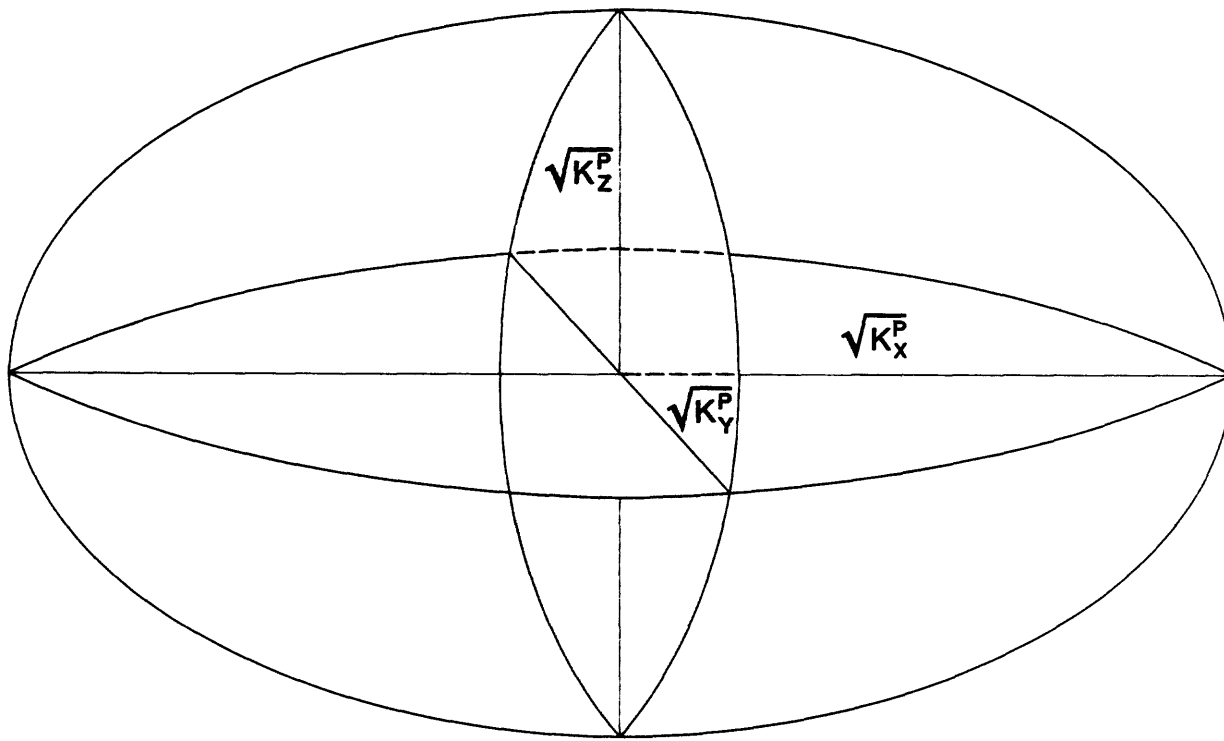
An anisotropic hydraulic-conductivity distribution in a localized volume may be described (Hsieh, 1983) as an ellipsoid whose axes are the square roots of the principal hydraulic conductivities (fig. 13). To determine the three principal directions, the ellipsoid will be described by two elliptical planes, one horizontal and one vertical (see figure 13). Values of hydraulic conductivity will be approximated for each plane by independent field-testing methods.

Values of vertical hydraulic conductivity will be calculated by methods of Weeks (1969) or Neuman (1975) in which the effect of vertical anisotropy on drawdown during aquifer tests is determined.

A method described by Papadopoulos (1965) and applied by Miller (1984) for nonsteady flow to a well in an infinite anisotropic aquifer will be used to determine principal values of horizontal hydraulic conductivity. Because the aquifer at the Bemidji site is unconfined, tests must be sufficiently long to assure horizontal flow at observation wells (E. P. Weeks, oral commun., U.S. Geological Survey, Denver, Colo.), and to minimize effects of lateral boundaries on the flow field. The methods described by Hantush and Thomas (1966) also may be used to determine anisotropy in the horizontal plane. A technique developed by Hsieh (1983) for determining the principal directions of hydraulic conductivity in three dimensions within fractured rocks also may be applicable after modification.

It may be possible to determine the principal directions of the hydraulic-conductivity ellipsoid by modifying test methods of Way and McKee (1982) in which three-dimensional hydraulic conductivity is determined in a homogeneous, anisotropic, leaky aquifer. A block diagram showing cross-bedding within tabular to wedge-shaped planar beds typical of glacial outwash deposits (Reineck and Singh, 1975) is illustrated in figure 14. Hydraulic-conductivity variations within each cross bed produce anisotropy within each planar section. Way and McKee (1982) suggest that the major component of the hydraulic-conductivity ellipsoid may be two to ten times greater than the minor components when cross-bedding is present.

Visual inspection of core samples from the Bemidji site and relative values of hydraulic conductivity from grain-size analysis by use of Hazen's formula (Hazen, 1930) indicate variability with depth that may be attributable to cross-bedding within planar units similar to those in figure 14 (D. I. Siegel, oral commun., Syracuse University, Syracuse, NY, 1984). Preliminary

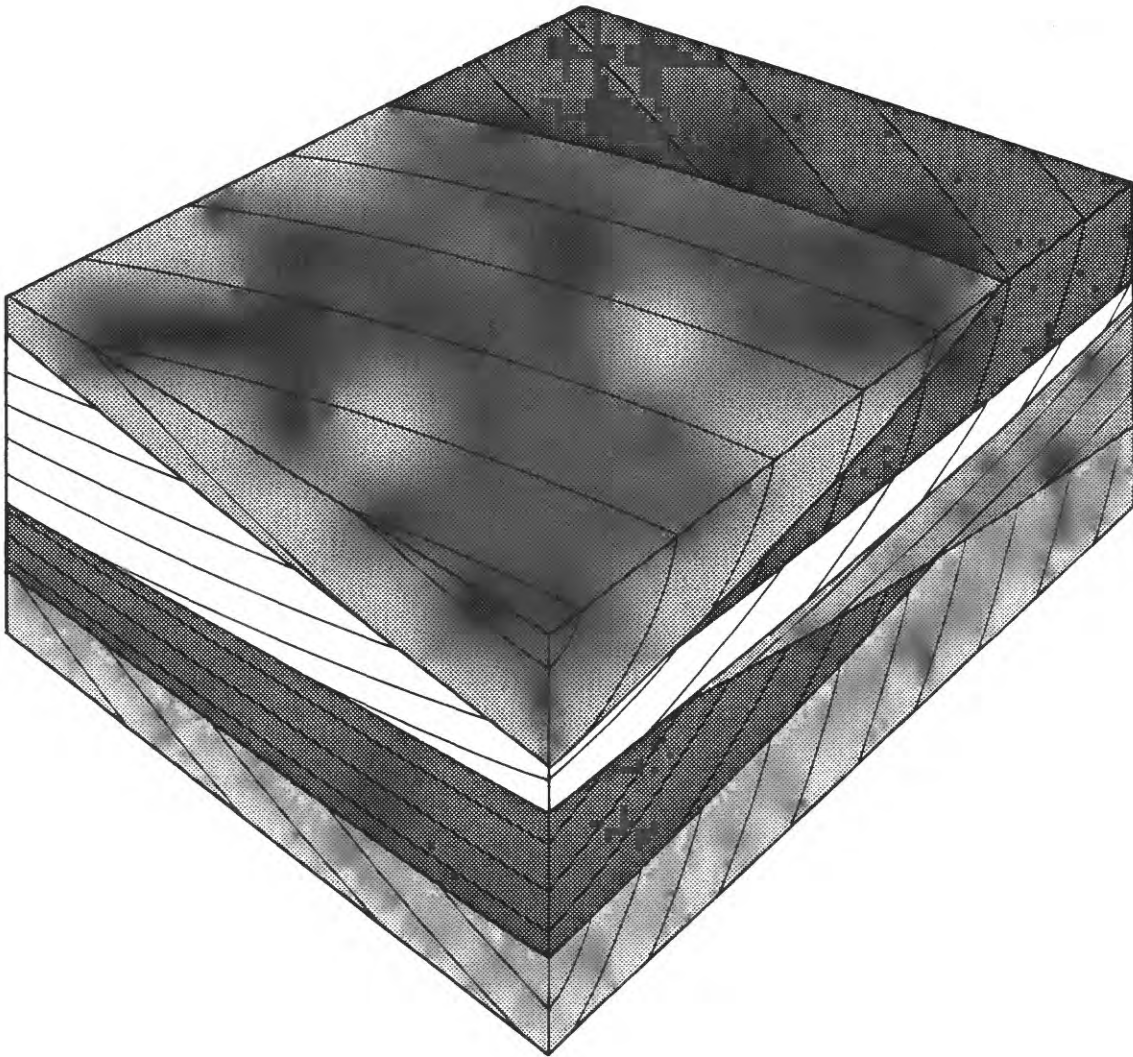


#### EXPLANATION

$\sqrt{K^P}$  Principal direction of  
hydraulic conductivity

x, y, z Axes direction

**Figure 13.--Principal directions of the hydraulic conductivity ellipsoid.**



***Figure 14.--Cross-bedding within planar bedding units.***

analysis of ground-penetrating-radar data indicates that planar beds are present in the unsaturated zone and likely also are present in the saturated zone (G. R. Olhoeft, oral commun., U.S. Geological Survey, Denver, Colo., 1984).

At the site, location and depth of observation and pumping wells for aquifer tests will be determined based on stratigraphy. Aquifer stratigraphy will be determined from geologic logs of test holes, from core samples, and from surface-geophysical techniques such as ground-penetrating radar and complex resistivity. Relative values of horizontal and vertical hydraulic conductivity will be determined by grain-size analysis of core samples and by laboratory permeameter tests. Aquifer porosity will be determined from gamma-gamma and neutron bore-hole geophysical logs.

#### **Determination of Field Dispersivity**

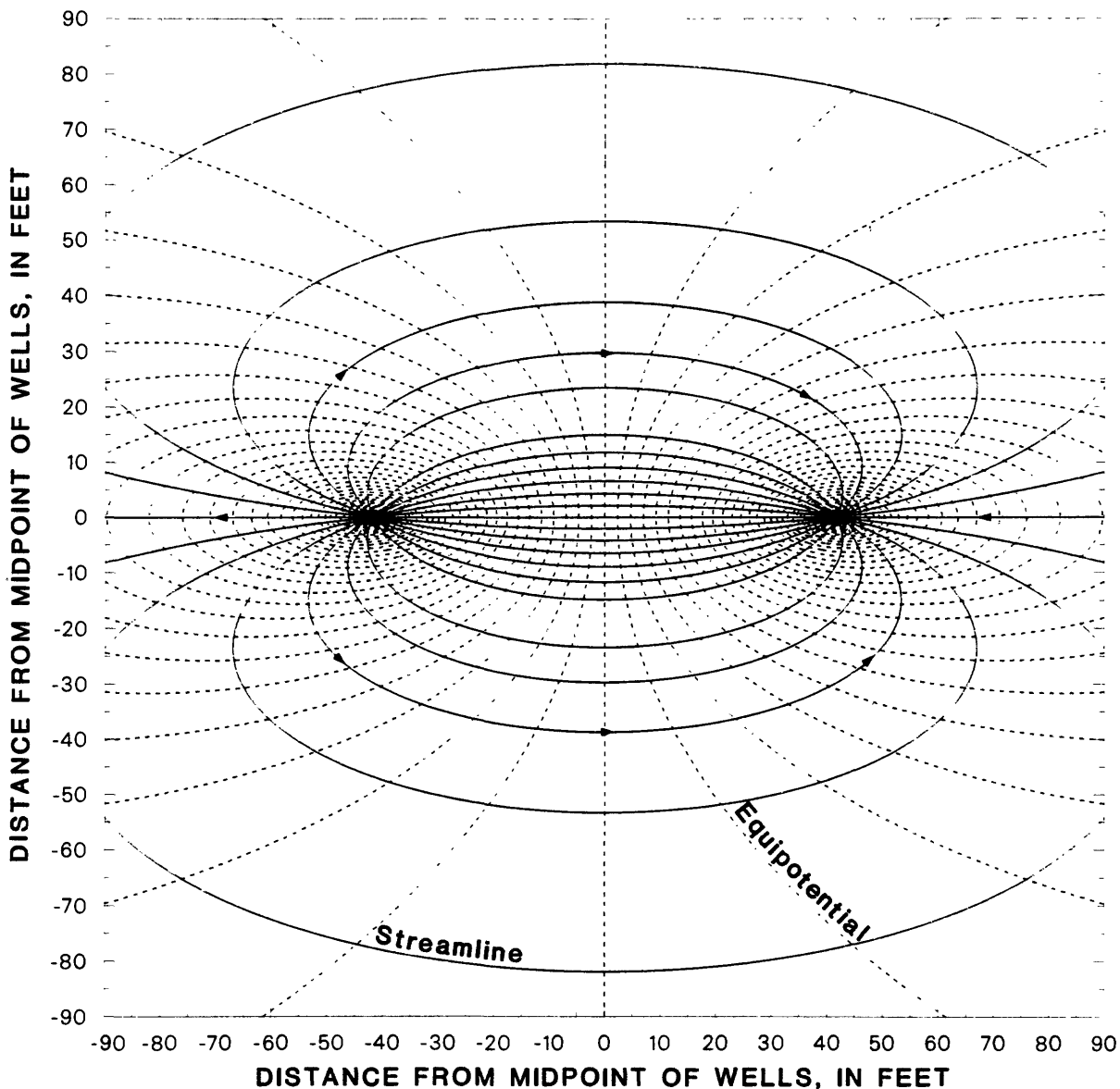
Dispersivity at the site will be determined by use of tracer-test data from single-well injection/withdrawal tests similar to those conducted by Sudicky and Cherry (1979) and Pickens and Grisak (1981), and from a doublet-well configuration similar to that described by Grove (1971), Sauty (1980) or Pickens and Grisak (1981). Observation wells used for determining hydraulic conductivity in three dimensions also will be used to observe tracer movement with additional wells located along the principal axes of horizontal hydraulic conductivity. A conservative anionic tracer such as  $\text{Br}^-$  (bromide),  $\text{I}^-$  (Iodide), or  $\text{Cl}^-$  (chloride) will be selected depending on local ground-water chemistry. Preliminary analysis of ground-water chemistry at the Bemidji site indicates low natural levels of chloride and suggests that  $\text{Cl}^-$  may be a suitable tracer. It may be possible to use neutron-activatable tracers as described by Hassler and others (1978), if the potential exists for reactions between the tracer and aquifer materials that will aid understanding of tracer movement and changes in concentration. Neutron-activation analysis allows multi-tracing, or the use of more than one tracer simultaneously, which can reveal sorption or chemical reaction of the tracer by the aquifer.

#### **Data Collection, Storage, and Analysis**

A self-contained, portable, computerized data-collection, storage and analysis system will be designed for field testing at the Bemidji site. The data-collection system will consist of pressure transducers to measure water levels continuously, digital flow meters to measure rates of injection and withdrawal continuously, and variable analog or digital input-signal capability to accommodate measurements of temperature and tracer concentration. Data will be stored at the site for real-time processing and also on removable magnetic disk for post-test analysis. Real-time data analysis will consist of computer programs that use cathode ray tube (CRT) or paper-output-graphics display for curve matching or for statistical least-squares minimization as described by Rayner (1980) or McElwee (1980). It also may be possible to modify the nonlinear least-squares-regression techniques developed by E. G. Lappela (unpublished report, currently being revised and edited by E. P. Weeks, U.S. Geological Survey, Denver, Colo.) for computer analysis of single-well injection or withdrawal tracer tests to determine longitudinal dispersivity.

## DETERMINATION OF HYDRAULIC CONDUCTIVITY AND ITS RELATION TO DISPERSIVITY

Many recent studies of dispersivity have reduced the three-dimensional field problem to two dimensions by assuming isotropic conditions in the horizontal plane of the hydraulic conductivity ellipsoid (see figure 13). Figure 15 illustrates the flow field for a doublet-well system for isotropic conditions in the horizontal plane (Bear, 1972) often assumed in two-dimensional studies. Field studies generally have concentrated on the scale-dependence of dispersivity in the horizontal plane and on variations in hydraulic conductivity with depth. Figure 14 suggests, however, that the same hydraulic conductivity variations that occur in the vertical plane also may occur in the



**Figure 15.--Flow field for a doublet-well system with isotropic conditions in the horizontal plane.**

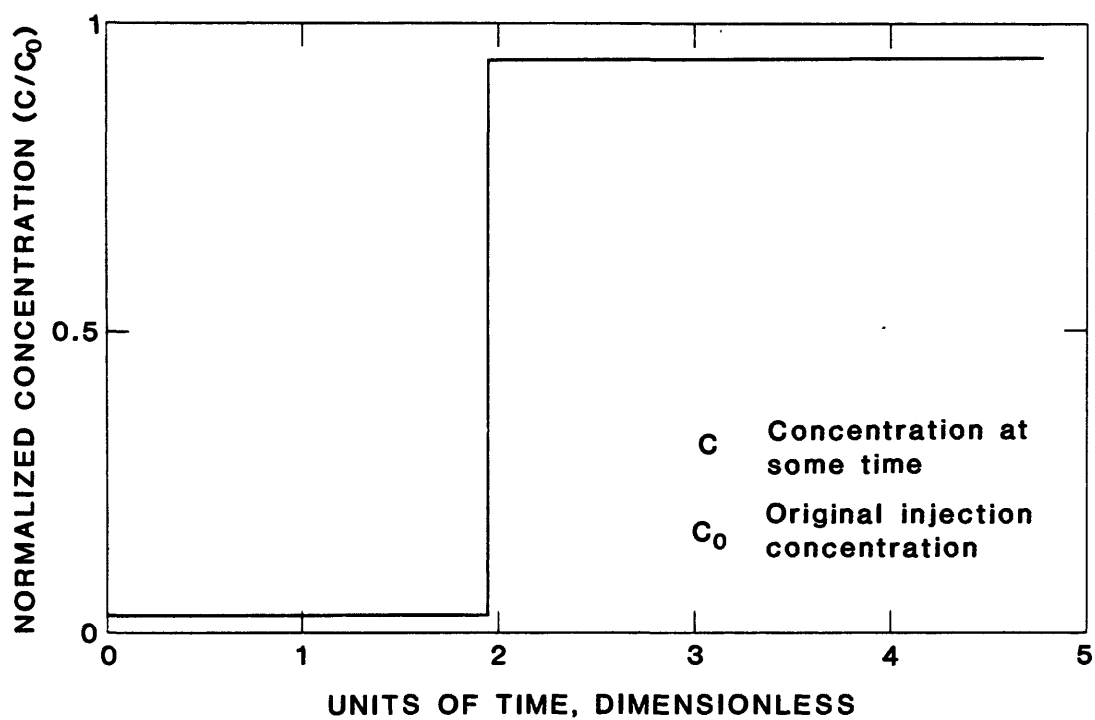
horizontal plane. The possible effects of these assumptions and observations on dispersion are discussed below.

Figure 16 shows a hypothetical, ideal-breakthrough curve at an arbitrary observation point for continuous injection of a tracer with no dispersion, and figure 17 is the ideal-breakthrough curve for continuous injection with dispersion where the value of concentration,  $C$ , is normalized by dividing  $C$  by the injection concentration,  $C_0$ . Comparison of figures 16 and 17 suggests that the dispersion process tends to flatten the breakthrough curves for continuous injection.

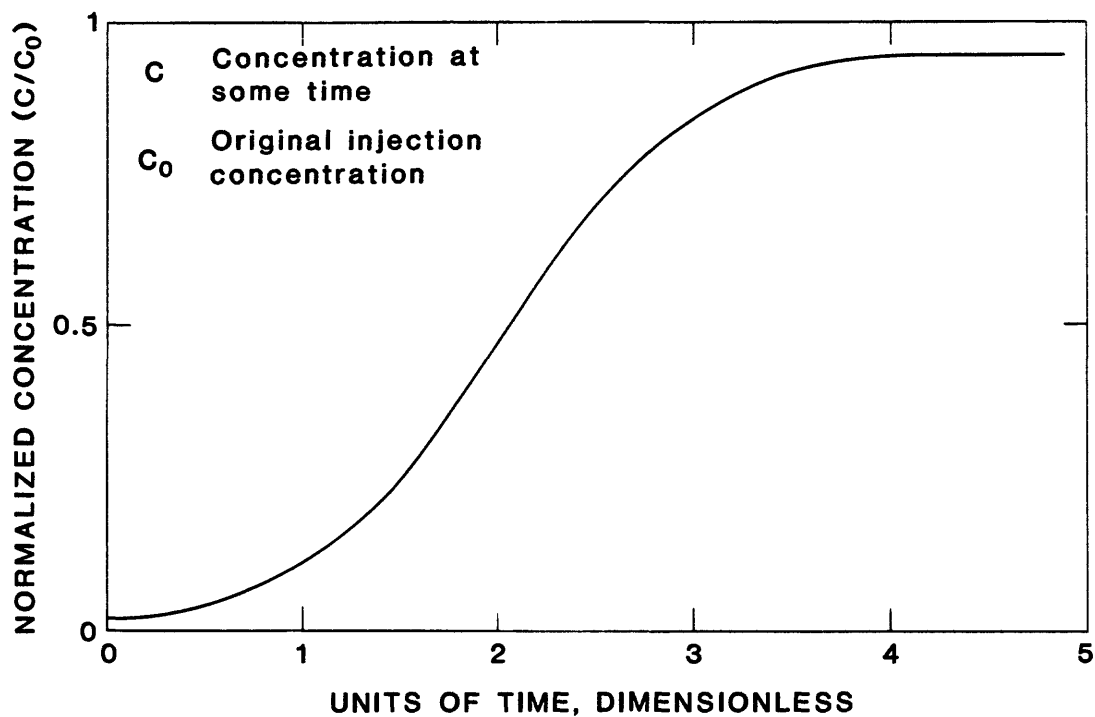
Figure 18 shows the hypothetical location of three doublet-well sets AB, AC, and AD. The diagram is oriented so that the block faces and well sets AB and AC are parallel to the three principal axes of hydraulic conductivity. Flow fields were determined for well sets AB and AC. Figure 19 illustrates the flow field for the hypothetical doublet-well set AB, where the axis through the wells is parallel to the major axis of horizontal hydraulic conductivity, and conductivity along the major axis is five times that along the minor axis. For most streamlines between the two wells, the distance traveled by a tracer particle is shorter for the anisotropic flow field (fig. 19) than it is for the isotropic flow field (fig. 15).

Figure 20 illustrates the flow field for doublet-well set AC, where the axis through the wells is parallel to the minor axis of horizontal hydraulic conductivity, and conductivity along the major axis is five times that along the minor axis. Comparison between figures 15, 19, and 20 indicates that, for most streamlines, the travel distance of a tracer particle is greatest for the doublet-well set AC, oriented parallel to the minor axis of horizontal hydraulic conductivity, and least for the doublet-well set AB, oriented parallel to the major axis of horizontal hydraulic conductivity.

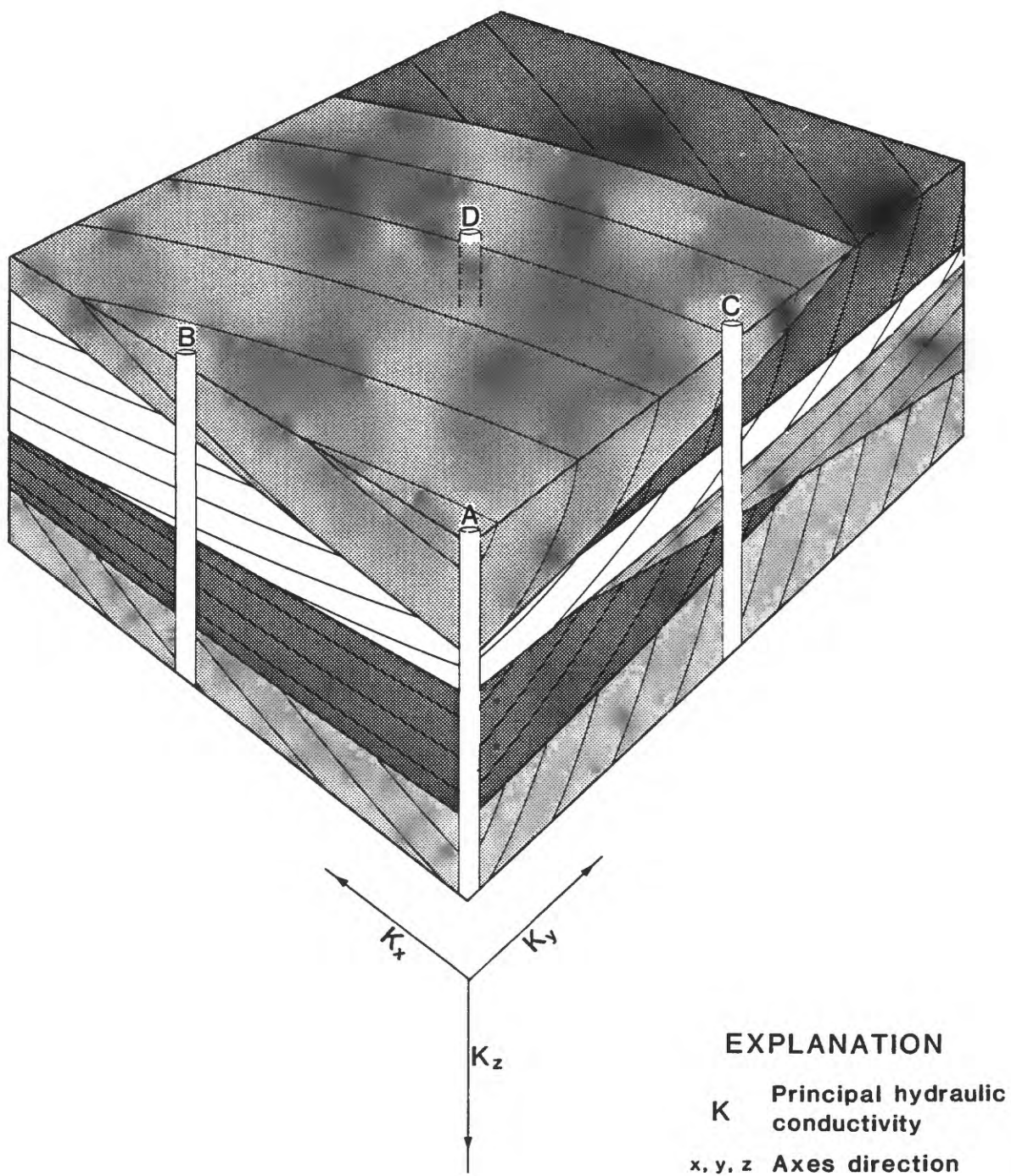
Given that dispersivity is a scale-dependent value related to the distance the tracer travels from the injection point to the observation point, the relative effect of dispersion on the ideal-breakthrough curve for continuous injection (fig. 17) can be determined. Recent doublet-well tracer studies by Pickens and Grisak (1981) suggest that the farther the tracer moves, the larger the value of field-determined dispersivity. Applying these results to the flow fields in figures 15, 19, and 20 suggests that the value of dispersivity is less for doublet-well set AB, which is oriented parallel to the major axis of horizontal hydraulic conductivity (fig. 19), than the dispersivity for the isotropic case (fig. 15). Similarly, the value of dispersivity is greater for doublet-well set AC, which is oriented parallel to the minor axis of horizontal hydraulic conductivity (fig. 20), than that for the isotropic case. The resulting hypothetical breakthrough curves for the isotropic and the two anisotropic doublet-well flow fields (AB and AC) are shown in figure 21. Note that for the doublet-well set AC, oriented parallel to the minor axis of horizontal hydraulic conductivity, the effect of dispersion on movement of a tracer is much greater than for the other doublet-well sets.



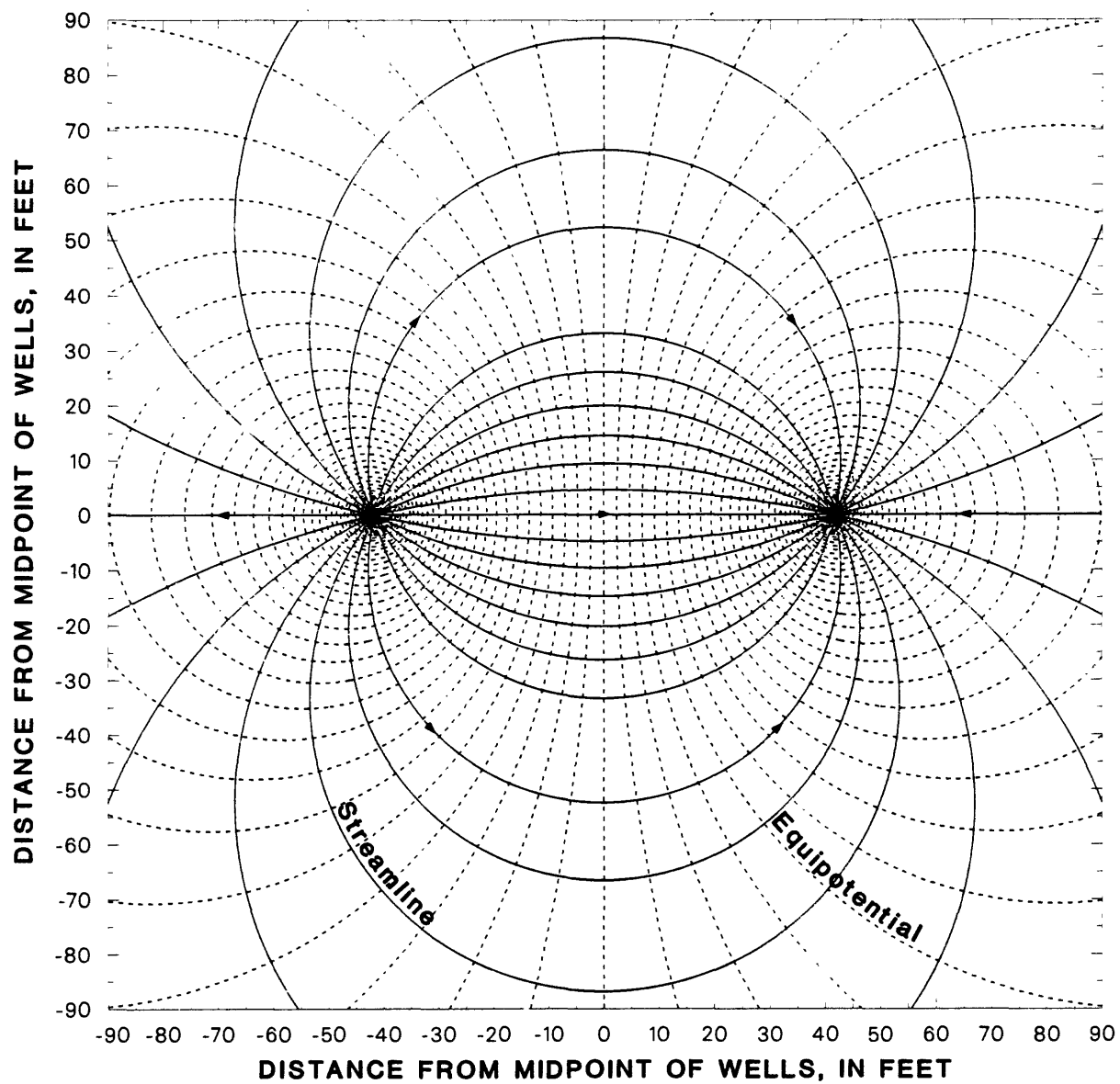
**Figure 16.--Hypothetical breakthrough curve with no dispersion.**



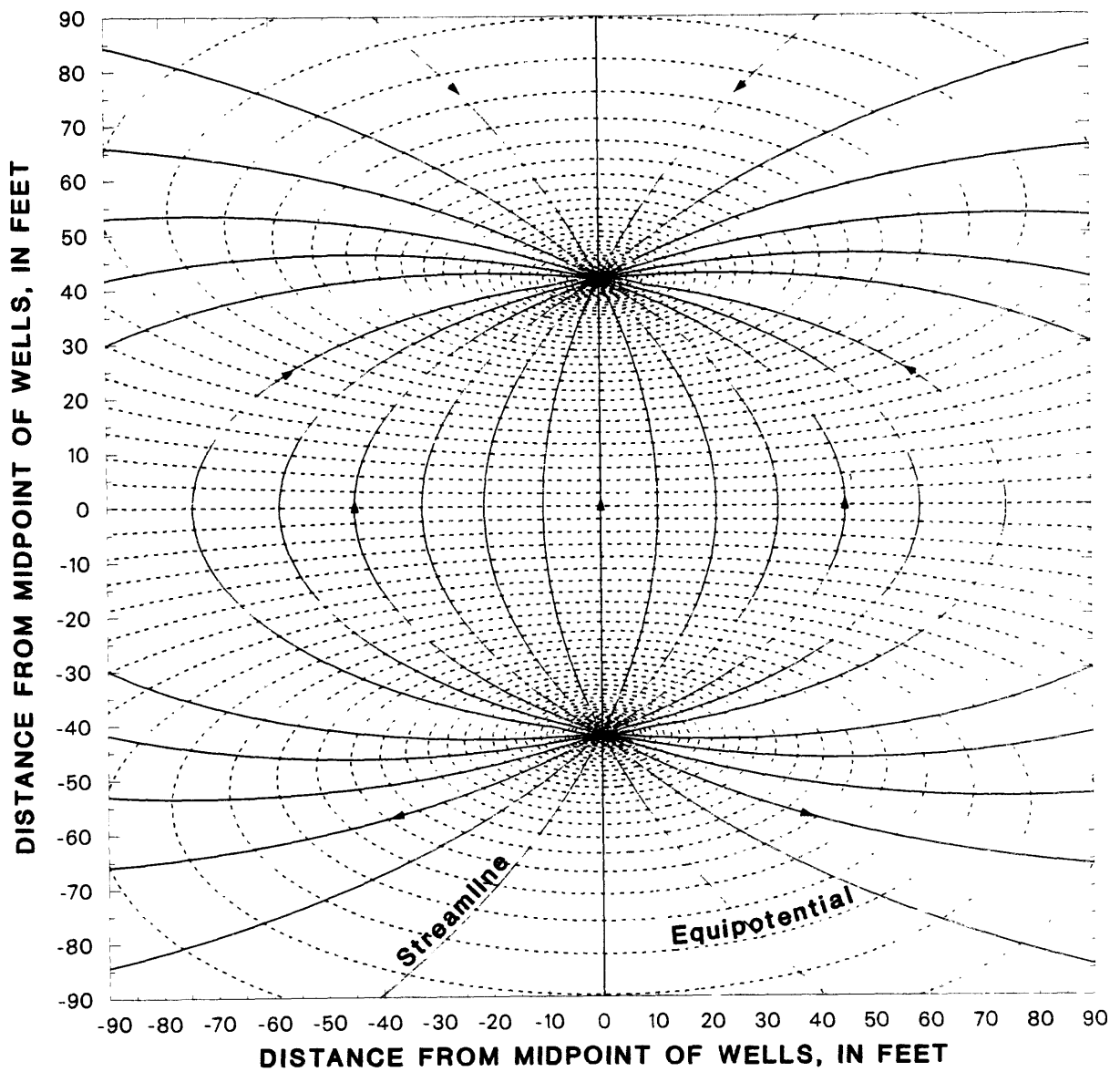
**Figure 17.--Hypothetical breakthrough curve with dispersion.**



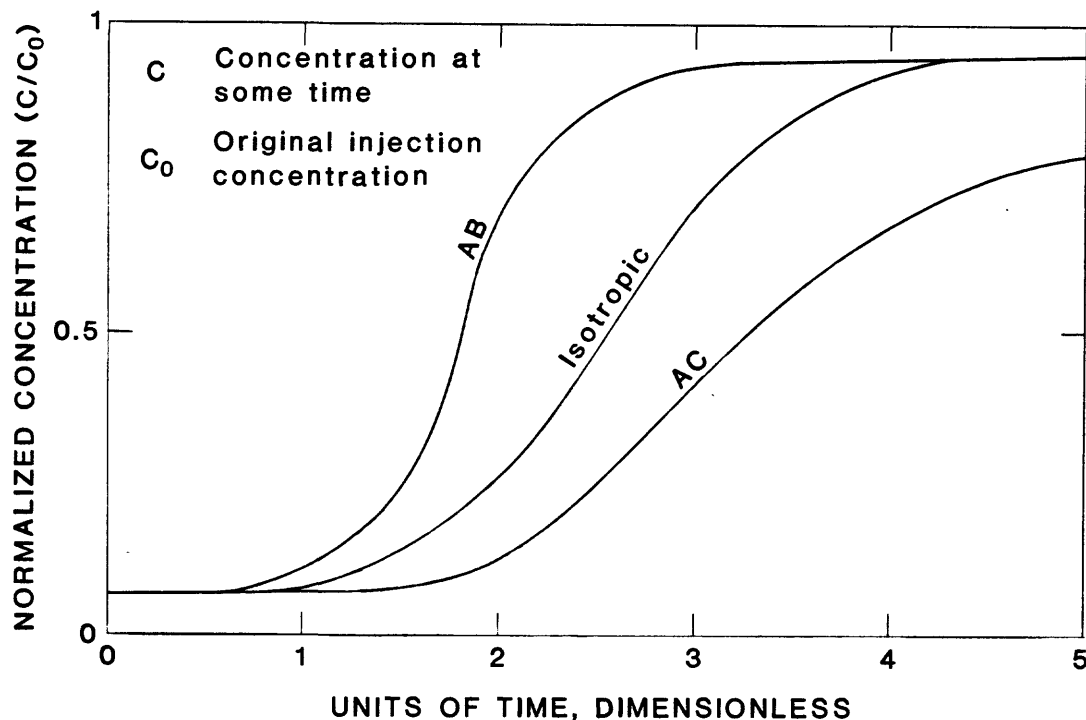
**Figure 18.--Hypothetical location of doublet-well sets aligned with the major axis of hydraulic conductivity.**



**Figure 19.--Flow field for the doublet-well set AB, where the axis through the wells is parallel to the major axis of horizontal hydraulic conductivity.**



**Figure 20.--Flow field for the doublet-well set AC, where the axis through the wells is parallel to the minor axis of horizontal hydraulic conductivity.**



**Figure 21.--Hypothetical breakthrough curves for isotropic and two anisotropic (AB and AC) doublet-well flow fields.**

#### **SUMMARY**

Recent investigations suggest that dispersion in aquifers is scale dependent and a function of the heterogeneity of the aquifer material. Stochastic analyses indicate that determining hydraulic conductivity in three dimensions is important in analyzing the dispersion process. Some investigators suggest that more emphasis is needed on field determination of hydraulic conductivity in three dimensions for describing the scale dependence of dispersivity, and less emphasis on incorporating somewhat arbitrary dispersion coefficients into complex mathematical models.

Although there are field techniques for determining hydraulic conductivity in three dimensions, the techniques generally are not used owing to the high cost of field equipment and the cumbersome and time-consuming methods for collecting and interpreting data manually.

The overall objective of the study is to test the hypothesis that field-determined values of dispersivity may be described as a function of hydraulic conductivity in three dimensions. The specific objectives of the research element for the Bemidji research site are to (1) determine hydraulic conductivity of the porous media in three dimensions, (2) determine the field value of dispersivity and its scale dependence on hydraulic conductivity, and (3) develop and apply a computerized data-collection, storage, and analysis system for field use in comprehensive measurements of hydraulic conductivity and dispersivity.

Hydraulic conductivity will be determined separately for the horizontal and vertical planes of the hydraulic-conductivity ellipsoid by proven techniques. It may be possible to modify other methods, such as those used to determine the principal directions of hydraulic conductivity in fractured rocks, and apply them to the outwash aquifer at Bemidji.

Observation wells for aquifer testing will be located based on stratigraphy of the aquifer determined from test-hole logs, core samples, grain-size analyses, bore-hole geophysics, and surface geophysics. Preliminary estimates of hydraulic conductivity from grain-size analyses suggests that the aquifer at the Bemidji research site is heterogeneous in the vertical plane due to cross-bedding. Ground-penetrating radar surveys suggest that planar beds, typical of glacial outwash deposits, are present at the Bemidji site.

Dispersivity will be determined in the field with data from standard single-well and doublet-well injection/withdrawal tracer-test. Observation wells will be located along the field-determined principal axes of horizontal hydraulic conductivity. A conservative anionic tracer such as  $\text{Br}^-$ ,  $\text{I}^-$ , or  $\text{Cl}^-$  will be injected depending on local ground-water chemistry. Neutron-activatable tracers also may be injected if the potential exists for reactions between the tracer and aquifer materials that would aid the understanding of tracer movement and changes in concentration.

A self-contained, portable, computerized data-collection, storage, and analysis system will be designed for field testing at the Bemidji site. The data-collection system will be able to continuously measure analog or digital signals for pressure, temperature, flow rate, and tracer concentration. Data storage will be both internal and on magnetic disk. Data analysis will be with real-time computer programs that produce cathode-ray-tube or paper output suitable for curve matching or statistical least-squares minimization curve matching.

Preliminary analysis of flow fields in the horizontal plane for a hypothetical doublet-well tracer test, under conditions similar to those expected at the Bemidji site, suggests that the orientation of the doublet-well sets with respect to the principal axes of horizontal hydraulic conductivity can affect the relative field-determined value of dispersivity. The flow field for a doublet-well set oriented parallel to the major axis of horizontal hydraulic conductivity results in lower relative dispersivity than in the isotropic case. The flow field for a doublet-well set oriented parallel to the minor axis of horizontal hydraulic conductivity results in higher relative dispersivity than in the isotropic case.

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## CHAPTER E

### **ORGANIC GEOCHEMISTRY OF CRUDE-OIL CONTAMINANTS IN THE SUBSURFACE:**

#### **PRELIMINARY RESULTS AND PROJECT PLAN**

By Mary Jo Baedeker<sup>1</sup>, Robert P. Eganhouse<sup>2</sup>, and Sharon S. Lindsay<sup>1</sup>

#### **ABSTRACT**

Sediments from an aquifer contaminated with crude oil northwest of Bemidji, Minnesota, were analyzed for extractable hydrocarbons to understand the processes that affect distribution of the organic compounds. The predominant compounds of the crude oil are aliphatic hydrocarbons and, in the C<sub>8</sub> to C<sub>32</sub> range, compounds of lighter molecular weight are more abundant. No preference exists in the crude oil for hydrocarbons of odd- or even-carbon chain length. The concentrations of hydrocarbons decrease significantly down-gradient from the oil-contaminated zone. Within 80 feet of a sampling site with an oil layer, the concentration of hydrocarbons decreases by a factor of 10<sup>3</sup> and, in some locations, the concentrations are at background levels of 2 to 3 ug/g sediment. The distribution of normal alkanes shows that the lighter molecular weight components are preferentially removed, probably by volatilization. Furthermore, downgradient from the oil-contaminated zone the unresolved complex mixture is a larger component of the aliphatic hydrocarbon fraction. The predominant hydrocarbons in the uncontaminated sediments are high molecular weight compounds (C<sub>20</sub> to C<sub>32</sub>) which have a marked preference of odd- to even-carbon chain length. No difference exists in the  $\delta^{13}\text{C}$  measurements of the organic carbon in oil-contaminated sediment and natural sediment.

Plans for additional work include: (1) identify molecular markers to differentiate between natural and oil-contaminated organic material, and (2) evaluating the relative significance of those processes responsible for altering the composition of petroleum in the subsurface.

#### **INTRODUCTION**

A crude-oil spill near Bemidji, Minnesota, occurred in 1979 and resulted in contamination of an outwash-sand aquifer. A history of the spill and description of the site are presented in another paper of this series (Hult, Chapter A). About 2,700 barrels of oil remained after the clean-up was completed, and some of this residual petroleum migrated to the water table. Ground water discharges locally to a small lake about 1,000 feet from the spill. How far the contaminants have traveled in the flow regime, however, is not known.

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This paper presents the results of a study to investigate the fate of the organic compounds in the subsurface. Core material was analyzed to compare the distribution of organic compounds in: (1) sediment contaminated with petroleum near the spill, (2) sediment downgradient from the spill which may show the effects of oil migration and alteration, and (3) sediment from a remote site that is not contaminated by petroleum but may contain natural organic material. The sediment collected and analyzed included the aquifer material, which is predominantly sand, and the oil and (or) water phases where they were encountered.

## **METHODS OF STUDY**

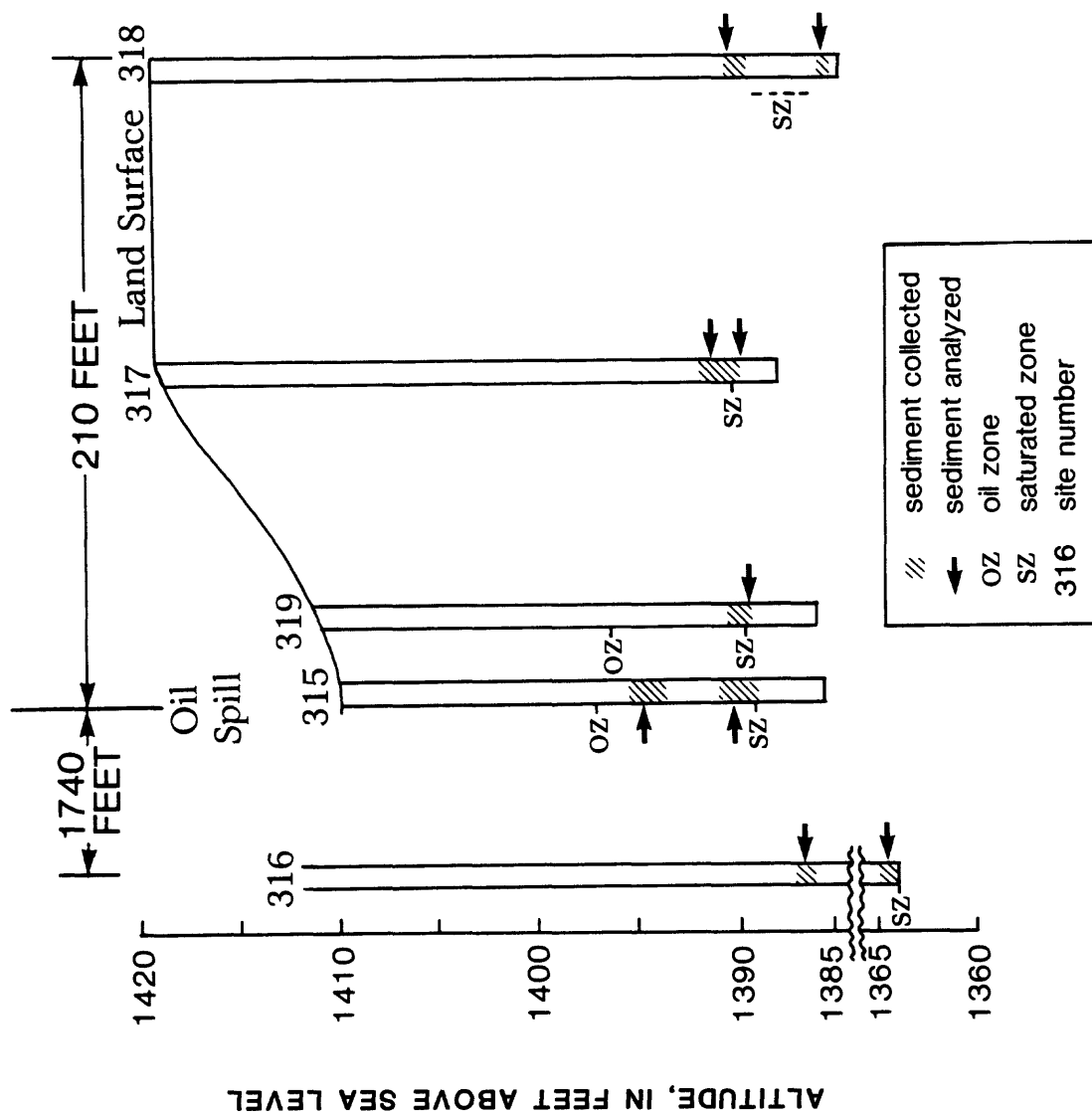
### **Sampling**

Sediments samples were taken at several sites near the spill and at a control site away from the spill. Samples were recovered with a split-spoon sampler that was lowered through a hollow-stem auger. The auger flights were steam cleaned before use. The split-spoon sampler was lined with methanol-washed brass liners to minimize organic contamination. The liners, with sediment intact, were frozen immediately with dry ice and returned to the laboratory for analysis. In addition, a sample of petroleum was bailed from a well at the spill site for analysis.

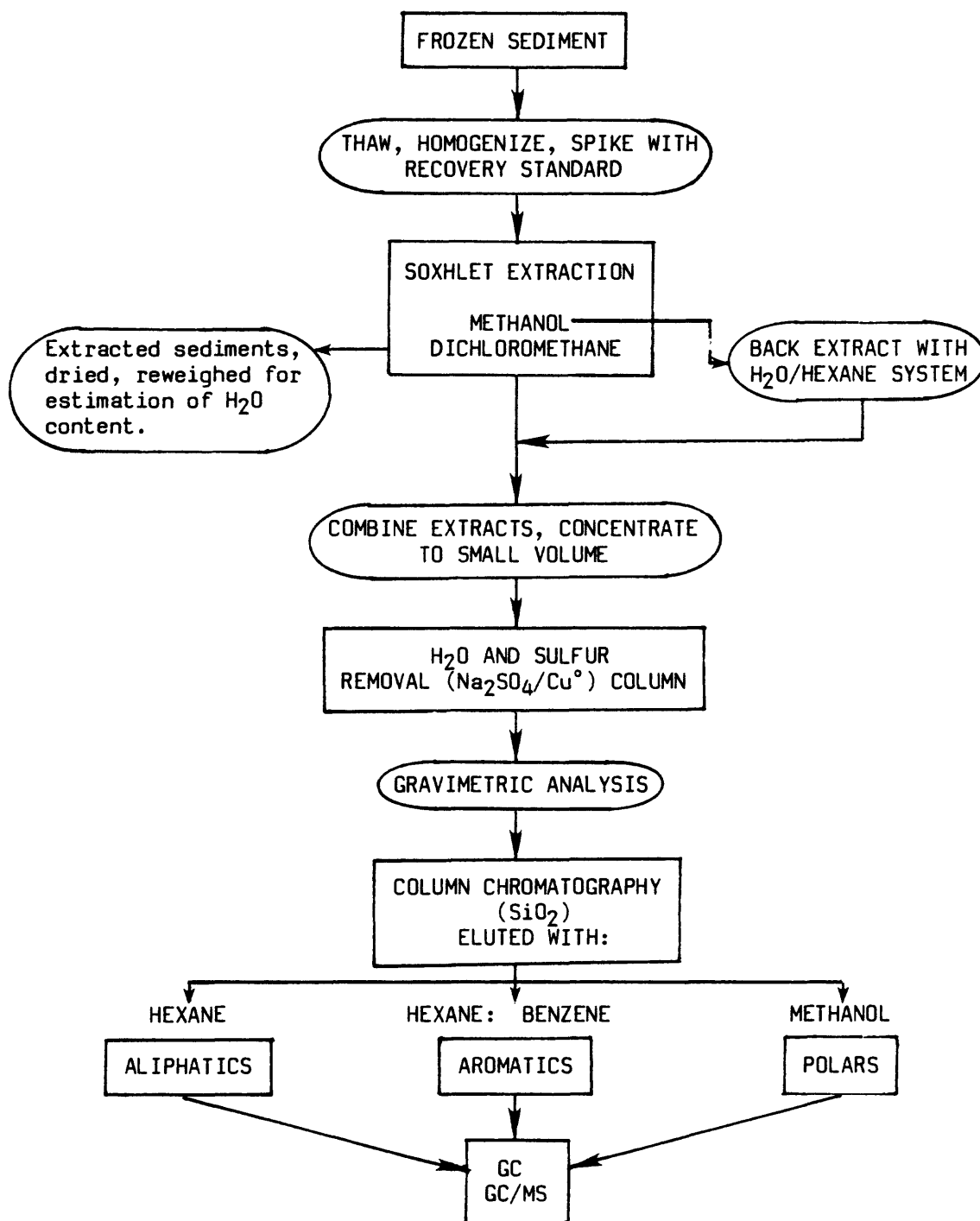
The sediment samples analyzed for hydrocarbons were taken from 4 sites 205 feet apart along the ground-water flowpath and at one control site about 1,700 feet upgradient of the spill. At sites 315 and 319 (fig. 22), the oily zone was between 10 and 15 feet below land surface. Although sediment recovered from site 317 had a petroleum odor, no separate oil phase was observed. At site 318, the sediment recovered had no discernible odor; however, after a well was installed, an odor of gasoline was detected in the well casing. The sediment interval recovered from the core is shown on figure 1 and the location of samples analyzed within the recovered sediment is marked. The samples analyzed from sites 315 and 319 were in the oil-contaminated zone above or near the saturated (water) zone. Samples analyzed from sites 317 and 318 were from both the unsaturated and saturated zones.

### **Extraction, Chromatographic Separation and Analysis**

The separation and extraction techniques used (fig. 23) were modified from Venkatesan and others (1980). After extraction of the frozen core, samples were thawed, homogenized, and spiked with a recovery standard and weighed into pre-extracted Soxhlet thimbles. The sediment was then extracted in a Soxhlet apparatus first with methanol to remove water and secondly with dichloromethane. The extracted sediment was dried at room temperature and weighed to estimate water content. Water was added to the methanol extract and the mixture was back-extracted with hexane. The combined hexane and dichloromethane solutions were concentrated to a small volume and passed through a sodium sulfate and activated copper column to remove water and sulfur. After concentration of the eluate to a known volume, small aliquots were analyzed gravimetrically for the content of extractable material. The samples were separated further by column chromatography on activated silica gel. The aliphatic hydrocarbons were eluted with one column volume of hexane;



**Figure 22.--Cross section of spill-site area showing the oil zone, saturated water zone, and location of sediments analyzed.**



**Figure 23.--Flow chart of procedures used for extraction, chromatographic separation, and analysis of hydrocarbons in sediments.**

the aromatic hydrocarbons eluted with two column volumes of a mixture of benzene and hexane; and the polars eluted with methanol. These fractions were analyzed by gas chromatography and mass spectrometry.

The extraction technique used to separate the hydrocarbons from the sediment results in the loss of volatile materials lighter than C<sub>12</sub>, thus the results for extractable hydrocarbons are limited to the range C<sub>12</sub> to C<sub>36</sub>. A standard mixture of normal alkanes was spiked into a precombusted sand sample. This "spiked blank" was processed along with the sediment extracts and provided a means of determining recovery and monitoring contamination levels. The concentrations of normal alkanes in sample extracts were corrected for recovery.

The fractions containing the aliphatic and aromatic hydrocarbons were evaporated under nitrogen and diluted with a known volume of hexane for analysis by gas chromatography. The samples were chromatographed on a Hewlett Packard<sup>1</sup> Model 4400 gas chromatograph using a J & W, bonded phase DB-5 capillary column and a splitless injection mode. The column was heated from 50°C to 300°C at 5° per minute.

The CPI (carbon preference index - table 4) is used to express the relative abundance of normal hydrocarbons having odd-carbon numbers (odd nC<sub>i</sub>) to those having even-carbon numbers (even nC<sub>i</sub>) by the following equation:

$$CPI = \frac{2 \sum \text{odd } nC_{21} \text{ to } nC_{31}}{\sum \text{even } nC_{20} \text{ to } nC_{30} + \sum \text{even } nC_{22} \text{ to } nC_{32}}$$

A CPI of one indicates no chain length preference. CPI's greater or less than one indicate a predominance of odd-numbered hydrocarbons or even-numbered hydrocarbons, respectively.

Stable isotope concentration measurements for <sup>13</sup>C were made on the organic carbon in the sediment. The <sup>13</sup> notation is defined by the following equation and measurements are reported relative to the-PDB standard:

$$\delta^{13}C = \left[ \frac{^{13}C/^{12}C \text{ sample}}{^{13}C/^{12}C \text{ standard}} - 1 \right] \times 1000$$

The organic material in the sediment was analyzed by two separate methods. In one method, organic material was extracted from the sediment with dichloromethane, the dichloromethane evaporated under nitrogen, and the remaining extract analyzed by combustion to carbon dioxide. In the other method, the sediment was treated with acid to remove carbonates, washed to remove the acid, and combusted to convert the organic material to carbon dioxide. In both methods, samples were combusted using a Leco instrument modified to purify and collect the gas for analysis by mass spectrometry.

<sup>1</sup> Use of a trade name in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

**Table 4.—Extractable hydrocarbons from Bemidji sediments**

Site	Total Extract <sup>1</sup> ng/g sediment	Total Aliphatic HC <sup>2</sup> ng/g sediment	CPI <sup>3</sup> nC <sub>21</sub> -nC <sub>31</sub>
315-15	12 x 10 <sup>6</sup>	5 x 10 <sup>6</sup>	1.0
315-20	34 x 10 <sup>6</sup>	12 x 10 <sup>6</sup>	1.0
319-21	54 x 10 <sup>6</sup>	21 x 10 <sup>6</sup>	1.0
317-28	20,000	3,620	1.0
317-29	<1,000	36	2.2
318-29	<4,000	700	1.2
318-34	3,000	600	1.2
316-47	<2,000	100	4.5

<sup>1</sup> Gravimetric analyses.

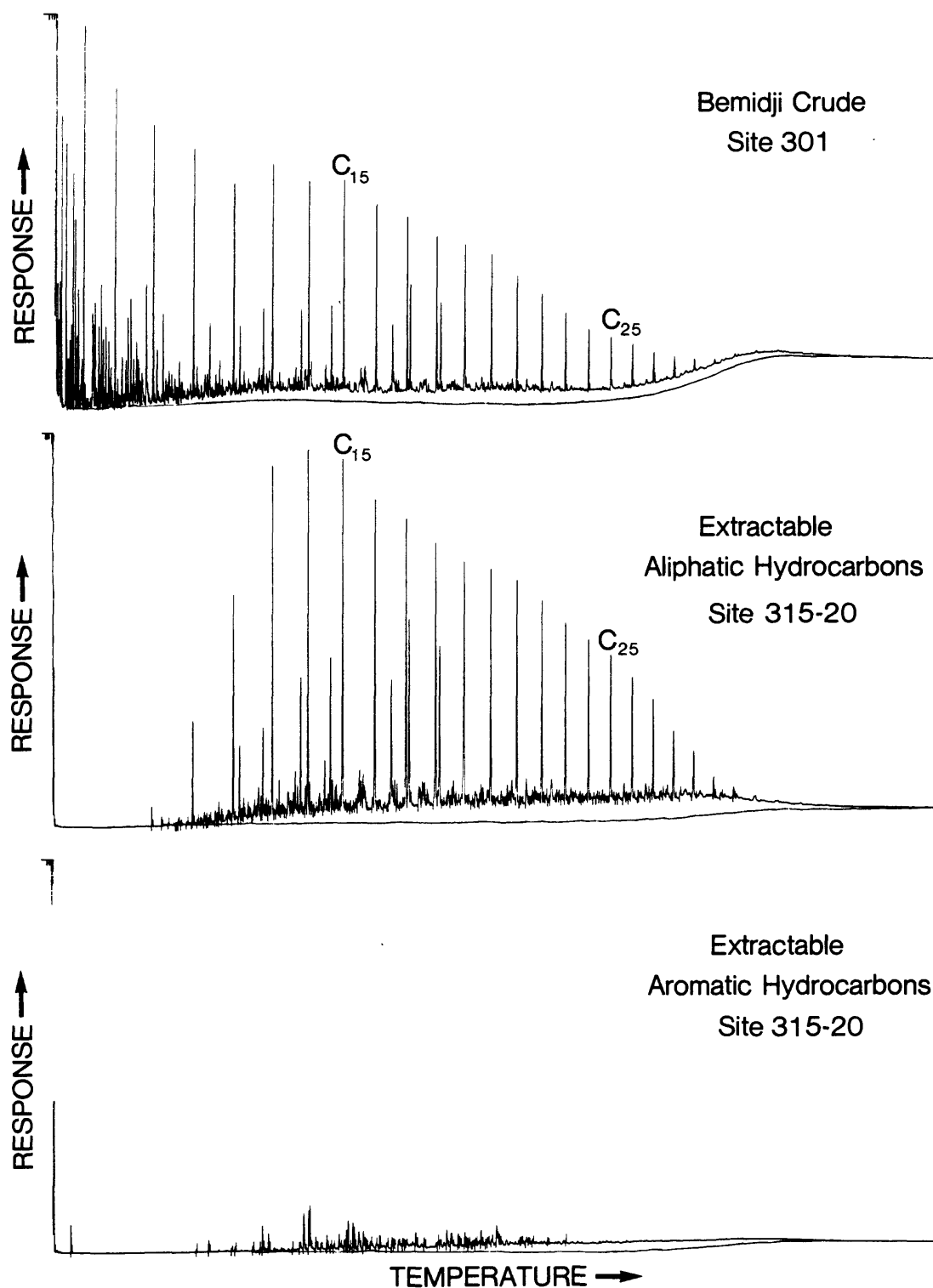
<sup>2</sup> GC analyses.

<sup>3</sup> Carbon preference index.

## RESULTS

A chromatogram of the Bemidji site crude oil shows that the predominant compounds are aliphatic hydrocarbons (fig. 24). Because octane (C<sub>8</sub> normal alkane) is the most abundant compound in the crude oil, it is highly likely that lower molecular weight compounds were also present in the crude oil and the sediments.

A comparison of the gas chromatogram of the total crude oil with those for the aliphatic and aromatic fractions of an oil-soaked sediment taken near the spill, shows that most of the compounds are aliphatic rather than aromatic (fig. 24). In the range of C<sub>12</sub> to C<sub>36</sub>, most of the compounds in the total crude oil can be accounted for by the normal alkanes alone. The baselines drawn on the chromatograms help indicate the relative amount of branched/cyclic compounds that are present as an unresolved complex mixture. This mixture is a sizeable part of the crude oil and of the isolated aliphatic and aromatic fractions. It is, also, in the extractable organic fraction of weathered petroleum, recent marine and lacustrine sediments that are polluted, and some older sediments. Thus, its presence in this environment is indicative of petroleum.



**Figure 24.--Gas chromatograms of crude oil at Bemidji and the aliphatic and aromatic hydrocarbons extracted from sediments in the vicinity of the oil spill.**

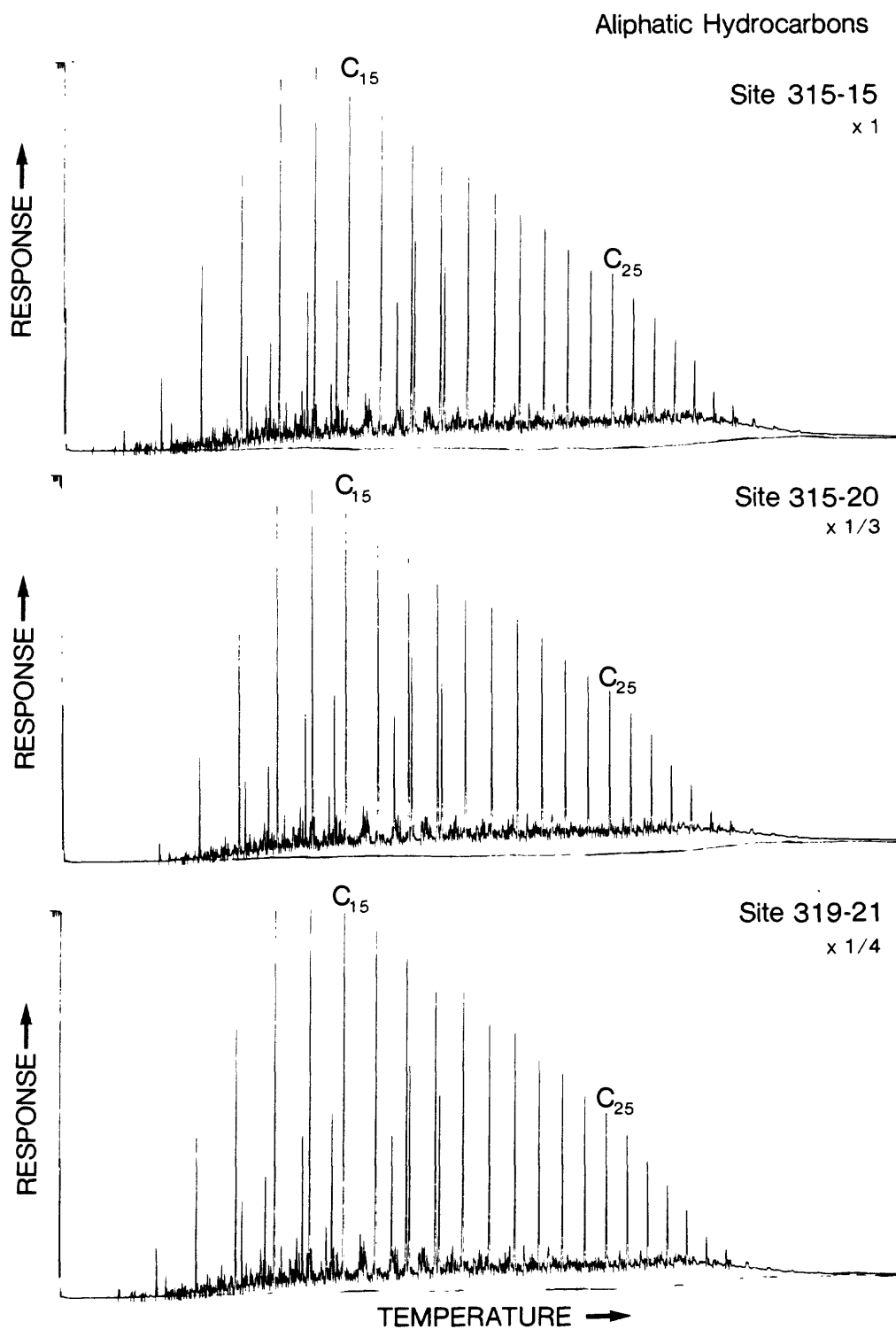
The concentration of total extractable organic material (table 1) decreases rapidly away from the oil-contaminated zone. Within 80 feet of the site where an oil layer was found, the concentration of hydrocarbons decreases by a factor of  $10^3$  and, in some locations, the concentrations are at background levels (2 to 3 ug/g). Also, the concentrations of aliphatic hydrocarbons decrease rapidly downgradient of the spill. Whereas the aliphatic hydrocarbons account for a major part of the organic material in the extracts of oil-coated sediments (sites 315, 319), this does not appear to be true for the other samples (sites 317, 318, and 316). Precise comparison of concentrations is difficult because the gravimetric data are only approximate for the small samples.

The distributions of aliphatic hydrocarbons from three oil-contaminated zones (sites 315 and 319) are nearly identical (fig. 25). Based on values corrected for recovery, the most abundant compound in all samples is normal  $C_{12}$  alkane. The branched hydrocarbons, pristane and phytane, which elute immediately after normal  $C_{17}$  and normal  $C_{18}$  alkanes, respectively, represent 3 percent of the total aliphatic hydrocarbons identified. These isoprenoid hydrocarbons are common constituents of petroleum. Other branched hydrocarbons are present, especially in the  $C_{12}$  to  $C_{17}$  region, but they have not yet been identified.

The distribution of aliphatic hydrocarbons in sediment 200 feet away from the spill (fig. 26, site 318-34) is quite different from that in the oil-contaminated zone. The most abundant compound is normal  $C_{19}$  alkane and the unresolved complex mixture is a much larger part of the total fraction. This suggests that hydrocarbons in sediment downgradient of the spill are depleted in the more volatile compounds. Furthermore, a significant part of all normal alkanes are lost, relative to the total amount of material in the aliphatic fraction. This could be accounted for either by evaporation of volatile compounds or by biodegradation.

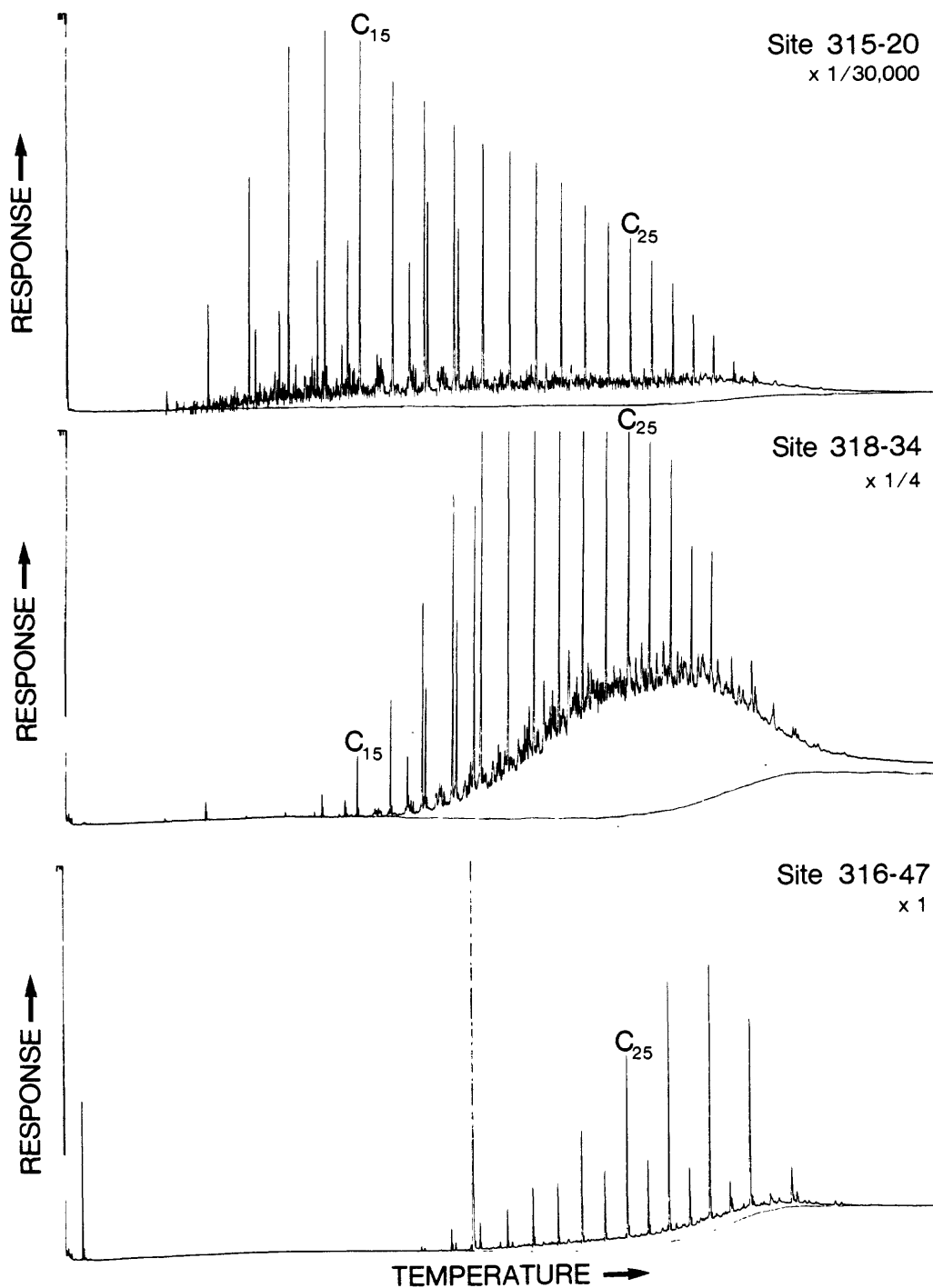
The biodegradation of crude oil results in the loss of total hydrocarbons in the  $C_{12}$  to  $C_{32}$  range. However, the normal hydrocarbons are selectively biodegraded relative to the branched hydrocarbons, such as pristane and phytane (Welte and others, 1982). Thus, if the loss of volatile hydrocarbons in the sediments downgradient from the spill were due to biodegradation, the ratios of the concentrations of pristane to  $nC_{17}$  and of phytane to  $nC_{18}$  should be higher than the same ratios of the original crude. These ratios show little variation, which suggests that biodegradation has not been a major process in altering the distribution of hydrocarbons.

The distribution of hydrocarbons in sediments from the control site (fig. 26, site 316-47) is different from the distribution in sediments near the spill. The most abundant compounds elute in the  $C_{23}$  to  $C_{33}$  region with hydrocarbons of odd-chain length predominating over hydrocarbons with even-chain lengths. This distribution is typical of terrestrial hydrocarbons derived from leaf waxes and is different from that found in the petroleum. A large peak close to  $C_{19}$  is an internal standard, which is not seen on other chromatographs because different dilution factors were used. Although the source of organic compounds at this site appears to be natural, small concentrations of the isoprenoid hydrocarbons, pristane and phytane are



**Figure 25.--Gas chromatograms comparing aliphatic hydrocarbons extracted from three sediments in the vicinity of the oil spill.**

Aliphatic Hydrocarbons



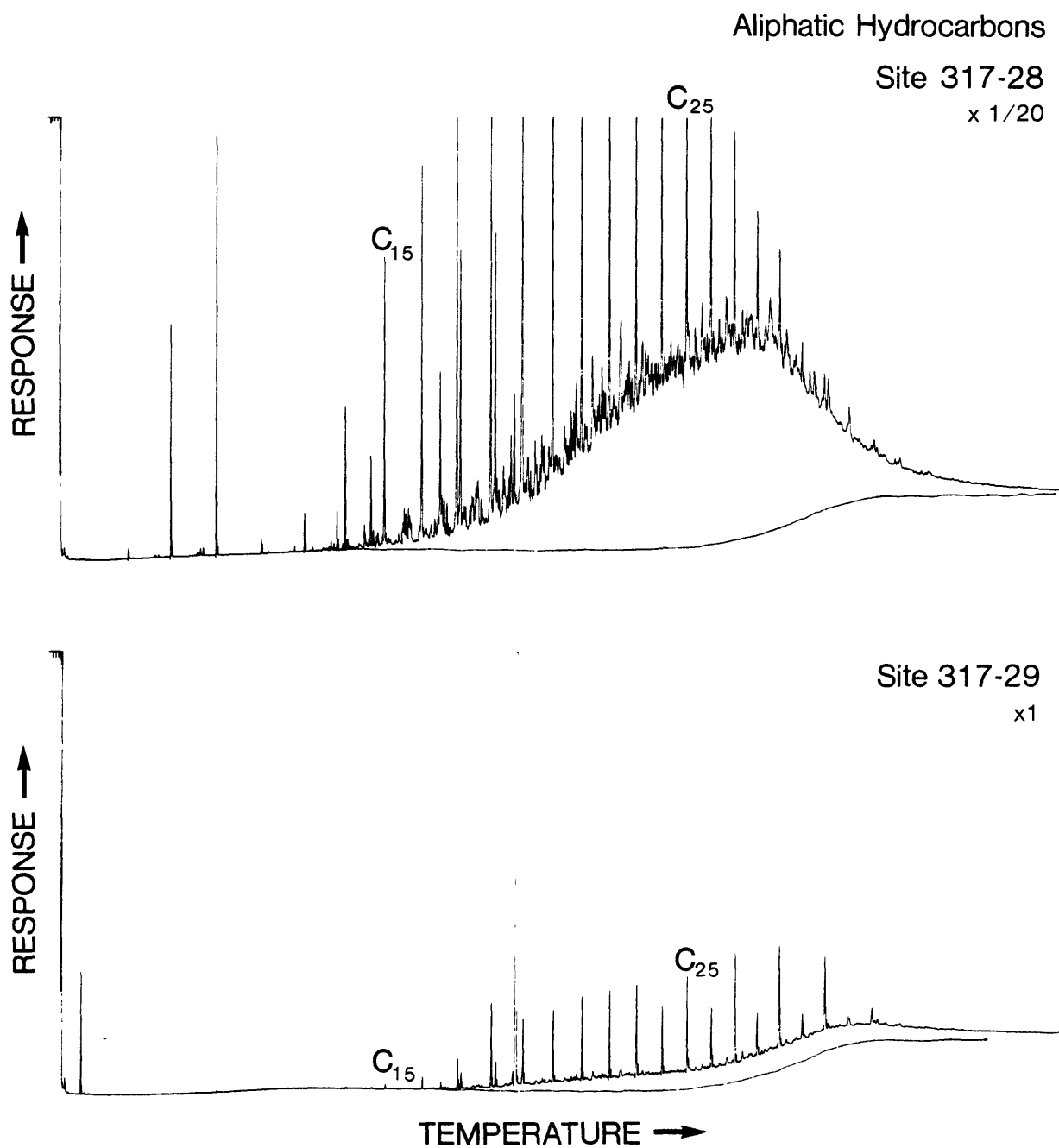
**Figure 26.--Gas chromatograms of the aliphatic hydrocarbons extracted from sediment near the spill, downgradient of the spill, and at a control site.**

present. These compounds are not usually found in pristine terrestrial environments. The presence of these compounds, in samples from the control site suggests that they may exist naturally. Alternatively, minute quantities of petroleum may have come from the drilling equipment or have been transported by air when the high-pressure pipeline broke.

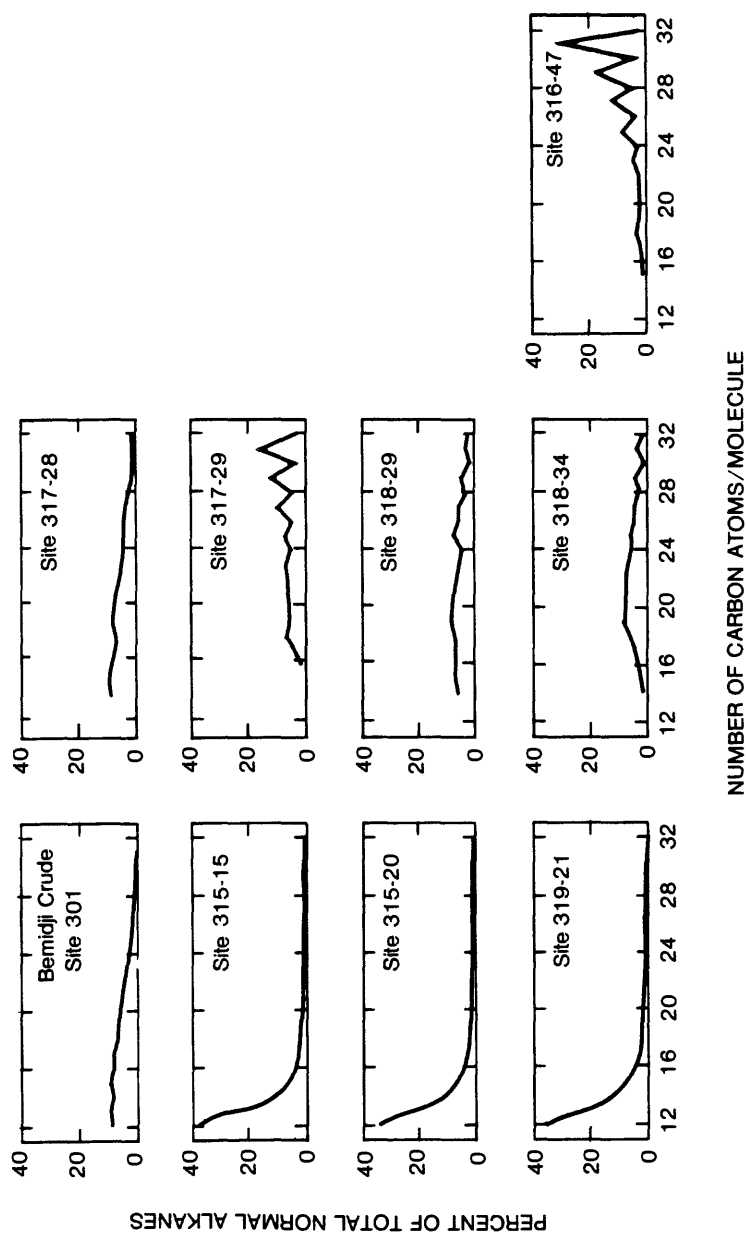
Major changes in the abundances of hydrocarbons are observed in the vicinity of the spill. The chromatogram for the aliphatic hydrocarbon fraction from site 317-28 is similar to that from site 318-34 and shows a loss of the more volatile constituents, an enhancement of the unresolved complex mixture, and a minimal contribution from terrigenous sources (fig. 27). However, the concentration of hydrocarbons extracted from sediment a foot deeper in the core (site 317-29), is lower by a factor of  $10^2$ . The distribution of normal hydrocarbons shows the presence of a mixture of both petroleum-derived and terrestrial hydrocarbons. The deeper sediment was from the saturated zone. The large differences in concentrations of hydrocarbons in sediments a foot apart in the subsurface suggests that the water table has not fluctuated significantly since the spill.

The distributions of normal alkanes ( $n_{C_{12}}$  to  $n_{C_{32}}$ ) in the sediments are shown in figure 28. The Bemidji crude oil and sample from site 316-47 serve as end members for the different types of organic material identified. The oil-contaminated sediments (sites 315-15, 315-20, and 319-21) show distribution patterns that are virtually identical. The fact that they appear to differ from the crude and show a stronger preference for the  $n_{C_{12}}$  and  $n_{C_{13}}$  alkanes is an artifact of the analytical methods; specifically, it results from correction for loss of n-alkanes during sample preparation. The crude oil was diluted with hexane and analyzed by gas chromatography directly without extraction or fractionation. Hence, no correction was necessary. All other samples were analyzed by the methods described earlier. Normal hydrocarbons in the oil sample and in extracts from the oil-contaminated sediments have a CPI of 1 (table 4), which indicates no preference of hydrocarbons with odd- or even-chain length. Normal hydrocarbons in sediment from the control site (316-47) show a predominance of higher molecular weight homologs and a strong preference of hydrocarbons with odd-carbon chain length (CPI of 4.5). In sediments down-gradient of the spill, the normal hydrocarbons are a mixture of the two types and have CPI's between 1 and 4.5.

On the basis of the  $\delta^{13}C$  measurements (table 5) there is little or no difference between the two sources of hydrocarbons. Although data are limited for the organic material in uncontaminated natural sediment in this area, the  $\delta^{13}C$  values for samples from sites 316-25 and 316-47 are similar to the values for the oil-contaminated sediment. Thus the  $\delta^{13}C$  values of the total organic material are not useful as a marker. Comparison of  $\delta^{13}C$  values for sediment analyzed by the two different methods, again, shows little variation. The acid-treatment method should result in losses of the volatile constituents. The extraction with dichloromethane would have the reverse effect of removing the lighter fraction from the sediment. At sites 315, 319, and 317 there is an apparent enrichment in the heavier isotope with depth in the acid-treated sediments; however, this is not seen at site 318. Loss of the more volatile components, which are generally slightly enriched in the lighter isotope (Silverman, 1963), could account for this difference.



**Figure 27.--Gas chromatograms of aliphatic hydrocarbons in sediment downgradient from the spill area in the unsaturated (317-28) and saturated (317-29) zones**



**Figure 28.--Distribution of individual normal alkanes in Bemidji crude oil and sediments as percent of total alkanes**

Table 5.—  $\delta^{13}\text{C}$  (‰) values of organic carbon in sediments

Samples	Untreated	Acid-treated	$\text{CH}_2\text{Cl}_2$ extracted
Contaminated sediment			
315-15		-29.15	-28.45
-20		-28.60	-28.75
-21		-25.90	
319-20		-29.35	-28.25
-21		-28.90	-28.70
317-28		-28.65	-28.70
-29		-27.05	
318-29		-29.05	
-34		-29.15	
Oil			
301	-28.40		
315	-28.55		
Natural sediment			
316-25		-28.83	
-47		-29.30	
Pond sediment		-27.34	

#### SUMMARY AND CONCLUSIONS

Petroleum in an unconfined aquifer is altered by several physical and chemical processes. After the oil seeps through the unsaturated zone and spreads laterally on the water table, it can be altered by chemical oxidation, thermal alteration, loss of asphaltenes, volatilization, biodegradation, water-washing, and sorption. Changes in the composition of petroleum due to chemical oxidation would be minimal because of limited oxygen and the short period of exposure. Likewise, thermal alteration would not be a major process in a near-surface aquifer because temperatures are relatively low and time is short. However, the most important processes by which petroleum is altered in the shallow subsurface are volatilization, biodegradation, water-washing, and sorption. In field studies, the distinction between these processes is not always readily discernable. For example, both volatilization and

biodegradation may selectively remove the more volatile components. Loss of asphaltenes may result from precipitation or by sorption on mineral surfaces or coatings.

The petroleum spilled at the Bemidji site is a light crude, composed predominantly of aliphatic hydrocarbons. The concentrations of individual compounds decrease rapidly away from the spill and the distributions of normal alkanes show that the organic material has been altered. The lighter molecular weight components are preferentially removed, probably by volatilization. Also, the total normal alkanes are selectively lost relative to the total aliphatic hydrocarbons, which results in an increase in the unresolved complex mixture. A short distance downgradient of the spill, the concentrations of petroleum hydrocarbons in the sediment approach the concentration levels of hydrocarbons from natural sources. Thus, the use of molecular markers is essential to differentiate between these sources. Although present in low concentrations, petroleum hydrocarbons were found in sediment about 200 feet downgradient from the spill. This is about one-fifth of the distance to the pond that is a local discharge point for ground water. It is possible that much of the area surrounding the spill may be slightly contaminated with hydrocarbons distributed by wind shortly after the spill.

Additional work will be done to identify molecular markers that will help distinguish between different sources of organic material. Compounds such as steranes, tricyclic diterpanes, pentacyclic triterpanes, and porphyrins may provide more information. Also, identification of specific aromatic hydrocarbons will be useful because the complex assemblages of these compounds typically found in petroleum are not generally present in terrestrial organic material. At specific sites, studies will be undertaken to determine the distribution of various compounds in the gas, water, and sediment phases to evaluate the relative significance of those processes responsible for altering the composition of petroleum.

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CHAPTER F  
**METHODS FOR THE IDENTIFICATION AND QUANTIFICATION OF  
ORGANIC COMPOUNDS IN CRUDE OIL**

By Rolland R. Grabbe<sup>1</sup>

**ABSTRACT**

A crude-oil-spill site near Bemidji, Minnesota, was selected for study of the migration and change in composition of organic compounds in crude oil. Plans are to develop qualitative and quantitative organic analytical methods to characterize crude oil into paraffins, olefins, naphthenes, and aromatics and to identify and measure the concentration of major individual compounds in the oil, ground water, and unsaturated zone. Analyses would be conducted using gas chromatography with flame ionization, mass spectrometer, and Fourier transform infrared spectrometer detectors.

**INTRODUCTION**

To describe the migration and change in composition of organic compounds present in crude oil spilled near Bemidji, Minnesota, accurate organic determinations must be performed on representative samples from the site. (For a description of the Bemidji research site, refer to Chapter A of this volume.) There are presently no methods approved by the U.S. Geological Survey for analysis of crude oil, of water samples contaminated by crude oil (one-phase), or of two-phase samples of water and oil. However, many organic analytical methods for these types of samples have been published in ASTM (American Society for Testing and Materials) manuals and other literature.

Organic analytical methods need to be developed within the Geological Survey for determining identities and quantities of compounds present in two-phase systems of water and oil. Individual compounds in crude oil in amounts greater than one-half percent by weight can be identified by gas chromatography/mass spectrometry (GC/MS) and gas chromatography/Fourier transform infrared spectrometry. Characterization of paraffins, naphthenes, aromatics, and olefins can be performed by GC/MS. Methods developed for these analyses will be transferred to the Survey's Central Laboratories for support of the Bemidji research project and other projects requiring these analyses.

Data from the analyses will be used by project members to help define the movement of crude oil and gases in the saturated and unsaturated zones of the aquifer.

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## Purpose and Scope

The purpose of this project is to develop and adapt methods for the qualitative and quantitative analyses of organic compounds in crude oil and crude-oil degradation products. Samples will be limited to crude oil, water, and gaseous samples at and near the spill site. Sampling and analyses will be coordinated with other project researchers and data provided to them.

### **PRESERVATION OF THE CRUDE-OIL SAMPLE**

After a representative sample has been collected, it must be "preserved" immediately to prevent degradation of any organic compounds. The preservation technique used must protect all compounds, not interfere with analyses, and be practical for on-site use. There is no single chemical additive that can preserve all compounds present in a complex mixture such as a crude-oil sample.

Rates of chemical reactions depend on temperature, concentration of reactants, nature of reactants, and catalysis. The easiest of these factors to control is temperature. The lower the temperature, the slower a chemical reaction proceeds. Furthermore, most biological activity stops just below the freezing point of water. Therefore, samples should be chilled to as low a temperature as practical as soon after collection as possible. For maximum preservation, dry ice ( $-78.5^{\circ}\text{C}$ ), which is obtainable almost anywhere (if necessary, from compressed  $\text{CO}_2$ ), is a good preservation agent which can be packed around samples for shipping. Samples from the Bemidji site should be stable indefinitely at  $-78.5^{\circ}\text{C}$ . [See ASTM Method D3325-78, "Preservation of Waterborne Oil Samples" (American Society for Testing and Materials, 1983d)].

When the water samples arrive at the laboratory, isolation of the organic compounds should begin as soon as possible. The sample, extracts, and any other fractions of the sample, should be stored at dry-ice temperature or lower to prevent degradation of the compounds.

### **ANALYSIS OF THE CRUDE-OIL SAMPLE**

#### Characterization of Crude Oil

A representative sample of the crude oil spilled at the Bemidji site should be diluted with methylene chloride and analyzed by GC/MS (operated by a data system). A fused silica capillary column should be used in the gas chromatograph to attain the best possible resolution of compounds in the crude oil. The crude-oil components would be identified and characterized by modifications of ASTM Method D2425-67 (American Society for Testing and Materials, 1983c). Complex inverse matrix calculations would be performed upon the summation of certain ions over all spectra. As many as 8,000 spectra may be acquired during the analysis of a single crude-oil sample.

Quantitation calculations of ASTM Method D2425-67 involve the summation of characteristic ions for a particular compound type, often called a "PNA" or a "PONA" analysis of crude oil or crude-oil derivatives where the letters P, O, N, and A stand for paraffins, olefins, naphthenes, and aromatics. Olefins are absent or almost nonexistent in crude oils and no calculations are included in

the ASTM method for determination of olefins. Olefins are present in refined petroleum products because of cracking and reaction processes. Table 6 lists a few of the summations used in ASTM Method D2425-67 to determine the different compound types.

**Table 6.—Mass spectra ions of crude oils that are summed to obtain hydrocarbon-type analyses for ASTM Method D2425-67 (American Society for Testing and Materials, 1983c)**

Hydrocarbon type	Summation performed on ions of mass/charge stated
Paraffins	$\sum 71 = 71 + 85$
Cycloparaffins	$\sum 67 = 67 + 68 + 69 + 81 + 82 + 83 + 96 + 97$
Alkylbenzenes	$\sum 91 = \sum_{N=0}^{N=6} [(91 + 14N) + (92 + 14N)]$
Indans and Tetralins	$\sum 103 = \sum_{N=0}^{N=6} [(103 + 14N) + (104 + 14N)]$
Indenes	$\sum 115 = \sum_{N=0}^{N=5} [(115 + 15N) + (116 + 14N)]$
Naphthalene	$\sum 128 = 128$
Naphthalenes	$\sum 141 = \sum_{N=0}^{N=7} [(141 + 14N) + (142 + 14N)]$
Acenaphthenes	$\sum 153 = \sum_{N=0}^{N=7} [(153 + 14N) + (154 + 14N)]$
Acenaphthylenes	$\sum 151 = \sum_{N=0}^{N=7} [(151 + 14N) + (152 + 14N)]$
Tricyclic aromatics	$\sum 177 = \sum_{N=0}^{N=7} [(177 + 14N) + (178 + 14N)]$

Because reproducible accurate analyses can be performed on synthetic mixtures by GC/MS, it may be possible to modify the method for crude oils so that the analyses can be routinely performed by the less expensive GC/FID (capillary gas chromatography using a flame ionization detector) method. Identification of some compounds can be made by retention time and quantitation performed from peak areas. The normal hydrocarbons generally are the major components of crude oil and can be identified by their retention times and their mass spectra. A complete series of normal hydrocarbons from pentane (5-carbons) through tetracontane (40-carbons) would be mixed together in a standard solution. This solution would be analyzed and used to obtain retention indices (Kovats indices) for all future analyses. Also, the mass spectra of each compound, with its appropriate header information, would be placed on a computer disc in a "user-generated" mass-spectral library for reference and identification purposes.

If chromatograms of the crude oils are too complex for separation of compound peaks, fractionation of the extracts must be performed by column chromatography using silica gel, aluminum oxide (alumina), or ion-exchange resins. Cleanup of the extracts, to remove high-molecular-weight materials, can be accomplished with macroreticular resins. Aromatic hydrocarbons can be separated from nonaromatics by elution chromatography using ASTM Method D2549-81 (American Society for Testing and Materials, 1983c).

#### Analyses of Single-Phase Water Samples

If the water sample seems to be homogeneous and does not have oil droplets or a sheen on the surface, routine analyses such as acid-base/neutral or purgeables (volatiles) can be performed without special treatment. For acid-base/neutral analyses, the sample is spiked with a mixture of surrogate compounds before extraction begins, and adjusted to at least pH 11 with potassium hydroxide solution, and a 1-liter sample is extracted with three 50-mL (milliliter) portions of methylene chloride. The extracts are combined, dried with anhydrous sodium sulfate, concentrated to 1.0 mL, spiked with an internal standard, labeled "base/neutral fraction," and analyzed. If base-sensitive compounds may be present, the sample is first extracted without pH adjustment by the same procedure just described and that fraction is called the "neutral fraction." After a neutral fraction is collected, the sample would be raised to at least pH 11 and extracted as described to produce a "base fraction." Then, in either of the above procedures, the pH would be decreased to 2 or less with sulfuric acid and the above procedure repeated to yield an "acid fraction." Each fraction would be analyzed separately. Combining fractions at this point can, at a minimum, cause differences in chromatography.

For purgeable (volatile) analyses, a 5-mL portion of sample is transferred to a sparging vessel that allows helium gas to be purged (bubbled) through the sample. The compounds that partition into the helium are carried with the helium into a trap packed with solid sorbent: Tenax GC<sup>1</sup>. The purgeable organic compounds contained in the trap are thermally desorbed and are carried

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<sup>1</sup> Use of the brand name in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

with the helium to the head of a gas chromatography column in a GC/MS system. The temperature in the column oven is programmed for the volatiles (purgeables) GC/MS analysis.

If detection levels below 1 ug/L (microgram per liter) are required for purgeable compounds, two different approaches can be pursued. The first approach is to increase the sample and sparging-vessel size, which will increase sensitivity 20 to 200 times. Closed-loop-stripping analysis is a second method that can be used to approach a detection limit in the nanogram-per-liter range for purgeable compounds.

Analyses of highly water-soluble organic compounds in the milligram-per-liter range can be accomplished for gas chromatographable substances by the direct aqueous-injection technique of ASTM Method D2908-74 (American Society for Testing and Materials, 1983a). High-performance-liquid chromatography can be used for thermally labile compounds that cannot be determined by gas chromatography.

Gas chromatography with a Fourier-transform infrared spectrometer can be used for isomer identification for gas chromatographable compounds, if isomer identification is necessary. This system is available in the U.S. Geological Survey Central Laboratory, Arvada, Colorado.

#### Analyses of Two-Phase Oil-Water Mixtures

It might be possible to separate the oil and water phases of a two-phase oil-water mixture by cooling or freezing the water. If the oil becomes viscous at 0° Celsius, the water could be decanted from the oil; otherwise, the water could be frozen and the oil layer poured from the water or washed away with methylene chloride.

If necessary, water can be removed from a crude-oil sample by ASTM Method D2560 or D2542 (American Society for Testing and Materials, 1983c). The water is removed by distillation-azeotropic distillation by the addition of a solvent such as xylenes.

Samples that do not form intractable emulsions can be extracted with methylene chloride. Continuous liquid-liquid extractors can be used to minimize emulsion formation.

If a sheen is observed on the water samples, it can be removed by dipping thin TFE-fluorocarbon strips in the sample to sorb the organic material using ASTM Method D3328-78 (American Society for Testing and Materials, 1983d). The strips are rinsed with solvent to wash off the organic material which then can be analyzed. If the sample contains an emulsion, a solvent such as pentane can be added to separate the phases, as described in ASTM Method D3414, Annexes A1 (American Society for Testing and Materials, 1983d). However, any foreign liquid added to the sample will alter the partitioning of organic compounds so the concentrations found in the different phases may not be in the same ratio as in the original sample.

## SUMMARY

During the methods development stage of the project, analyses will be performed on samples from the Bemidji research site. Data from these analyses will be provided to researchers working on the Bemidji project for their interpretation and use. The method will be modified so that it will be suitable for use by the Central Laboratories of the U.S. Geological Survey.

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## CHAPTER G

### **INORGANIC GEOCHEMISTRY OF GROUND WATER AND SEDIMENTS IN AN AQUIFER CONTAMINATED BY CRUDE OIL: PRELIMINARY RESULTS AND PROJECT PLAN**

By Donald I. Siegel<sup>1</sup> and David A. Franzi<sup>2</sup>

#### **ABSTRACT**

An investigation is proposed to study the effects of a spill of crude oil on the inorganic chemical system of a drift aquifer near Bemidji, Minnesota. This part of the study will evaluate the speciation and mobility of inorganic chemical constituents and their effects on ground-water quality. The hypothesis to be tested is that the organic contaminants and their by-products may alter the quality of ground water by (1) remobilizing chemical constituents contained within labile minerals or within organic materials in the drift, (2) behaving as a source for various trace constituents and nutrients, and (3) modifying rates of dissolution of aquifer sediments. Methods to be used include x-ray diffraction, sedimentary petrography, scanning-electron microscopy, chemical analyses of selected minerals, and selected leaching experiments.

Preliminary results of particle-size analyses indicate that the aquifer materials consist of poorly sorted medium sand with a range in hydraulic conductivity from about  $0.4 \times 10^{-4}$  to  $2.7 \times 10^{-4}$  meters per second. Analyses by x-ray diffraction indicate that the principal rock materials are quartz, calcite, dolomite, feldspar, and by point counting.

#### **INTRODUCTION**

The U.S. Geological Survey has begun a detailed investigation of the effects of a crude-oil spill on the geochemistry of an unconfined glacial outwash aquifer near Bemidji, Minnesota. Since the spill in August 1979, the contaminants have percolated to the water table and are moving through and reacting with the aquifer system. A description of the site, including its geologic and hydrologic setting, is given in Chapter A of this report.

Ground-water and sediment geochemistry at the Bemidji research site is related to the presence of the crude oil and to rates of chemical mass transfer from mineral phases and amorphous solids in the drift to the ground water. In addition to organic contamination found in the main body of the plume, residual, water-soluble, and gaseous by-products may be generated from in-situ

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chemical and biochemical degradation of the petroleum (Van der Waarden and others, 1977; Ehrlich and others, 1982, 1983). The petroleum and by-products may significantly alter water chemistry by mobilizing metals bound to exchangeable sites on clay minerals, behaving as a source for trace constituents and nutrients, and modifying rates of dissolution of aquifer sediments. The rate and nature of mass transfer of constituents from solids to water are functions of the native ground-water quality, degree of contamination, and mineralogical composition of the drift.

Although the controls on mineral dissolution are not completely understood (Aagaard and Helgeson, 1982), kinetic rate constants from numerous experimental studies on silicate minerals (Luce and others, 1972; Busenberg and Clemency, 1976; Siegel and Pfannkuch, 1984a) and on carbonate minerals (Plummer and others, 1979) can be used qualitatively to model inorganic mass transfer from complicated mineral assemblages to water. To date, the consideration of kinetics in water-quality models of glacial deposits has been essentially restricted to surface-water systems (Siegel, 1982), although the effect of kinetics on concentrations of major solutes in bedrock aquifers has been investigated (Palciauskis and Domenico, 1976; Claassen and White, 1979; Claassen, 1981). The effect of petroleum on the kinetics of dissolution has not been addressed in any study.

The study of inorganic sediment-water interactions at the Bemidji research site provides a unique opportunity to test whether inorganic trace constituents are significantly released as a by-product of petroleum decomposition. In particular, petroleum may be a significant source of halogens, which normally are considered to move conservatively within ground-water-flow systems (Hem, 1970).

This paper describes a work plan to investigate (1) the effects of the petroleum contaminants and their by-products on the quality of ground water, (2) sources and sinks of chemical constituents, and (3) rates of chemical mass transfer from solids to solution. Contamination by organic compounds may modify the geochemical partitioning of chemical constituents bound to exchangeable sites on clay minerals, sorbed to iron and manganese oxides and sesquioxides, and complexed with natural organics in the glacial drift. The contamination also may modify mineral dissolution rates and the stoichiometry of mass transfer during dissolution.

Evaluation of the inorganic geochemistry of the site will include detailed textural, mineralogical, and chemical analyses of the glacial drift. The chemical analysis will include whole-rock and selective dissolution methods, which will identify elements likely bound to exchangeable sites on clay minerals, in iron and manganese oxides, in carbonate and silicate minerals, and complexed with organic material. These data, combined with data on water quality, will allow the evaluation of the effects of petroleum contamination on processes that control the inorganic composition of the ground water.

#### **OBJECTIVES OF WORK PLAN**

The major objective of the Bemidji study is to evaluate the effects of contamination by crude oil on inorganic geochemistry in a shallow, unconfined

aquifer. Water-quality data, chemical analyses of the crude oil, isotopic data, and site information will be provided by the U.S. Geological Survey. The research effort at Syracuse University and Lafayette College will include the activities listed below.

1. Determination of the particle-size distribution of aquifer materials. Fine-grained sediments are more reactive because of greater surface-area to volume ratios. Grain-size data will be used empirically to estimate intrinsic permeability, an important hydraulic characteristic for evaluating residence time of ground water.
2. Determination of the chemical composition of the drift. This information will be used to determine if net mass transfer from solids to water phase is congruent or incongruent, and the chemical losses and gains along major flow paths. Selective leaching experiments will be designed to determine the chemical partitioning of constituents in the solid phases.
3. Determination of the mineralogic composition of selected size fractions of aquifer materials. These data will be useful for calculating mass transfer from solids to solution. Results from parts 2 and 3 will permit evaluation of the extent to which dissolution of carbonate minerals dominates the inorganic quality of the native ground water.
4. Determination of discontinuities and precipitated solid phases on grain surfaces. This information will aid evaluation of metal-exchange capacities of drift materials relative to clay minerals in the drift and the location in the ground-water-flow system where most dissolution occurs.

#### **APPROACH TO WORK PLAN**

Representative samples of drift collected along flowpaths adjacent to and through the contaminant plume will be analyzed by a variety of sedimentological and geochemical methods. Particle-size analyses will be done by standard sieve and pipette methods (Folk, 1974). Size data will be used by personnel of the U.S. Geological Survey research team to determine intrinsic permeability (Hazen, 1930; Krumbein and Monk, 1942; Masch and Denny, 1966) for comparison to field determinations of hydraulic characteristics.

X-ray diffraction analyses of the fine-grained fractions of the drift will be done with a Norelco<sup>1</sup> diffractometer using Ni-filtered CuK radiation (Carrol, 1970). Oriented slides will be prepared using the sediment-smear technique (Gibbs, 1965). These data coupled with petrographic point counts of selected sand fractions (Krumbein and Pettijohn, 1938; Milner, 1962) will be used to quantify the mineralogical composition of the aquifer materials. The chemical composition of the drift (bulk) and of individual minerals will be

determined by Direct-Current Plasma-Emission Spectrometry (Beckman<sup>1</sup> Spectrospan V DCP Spectrometer). Samples will be placed into solution by standard methods (Medlin and others, 1969). Individual minerals will be selected from the appropriate fractions in the drift for analysis. Inorganic carbon will be determined by a Perkin-Elmer<sup>1</sup> Analyzer equipped with a carbonate kit.

Chemical partitioning of constituents among five chemical fractions will be investigated:  $MgCl_2$  extractable, acetic-acid extractable, acidified hydroxylamine hydrochloride extractable, acidified hydrogen peroxide extractable, and residual material. Experimental studies have shown that this procedure approximately differentiates constituents bound to exchangeable sites on clay minerals, and in carbonate minerals, amorphous sesquioxides, organics, and residual silicate and oxide phases, respectively (Chester and Hughes, 1967; Tessier and others, 1979, 1982). These data should provide insight into the organic and inorganic availability, mobilization, and transport of chemical constituents in the study area.

Although most of the analyses will be for major elements, selected trace metals will be determined for bulk samples and individual minerals to evaluate likely sources for dissolved trace metals in the ground water and the provenance of the drift (Franzi, 1983). Trace metals to be determined will depend on the mineralogical composition of the drift and the trace metals identified in samples of the ground water and crude oil.

Scanning electron photomicrographs will be made of grain surfaces of the major mineral species to help determine the extent of dissolution of clays and other precipitate minerals. The photomicrographs also will aid identification of etch pits on silicate minerals where dissolution predominantly occurs (Berner and Holdren, 1979; Berner and Schott, 1980).

The mineralogical and geochemical data on the solid phases will be used with ground-water-quality data from nested wells along the flowpaths to conceptually model the evolution of ground-water quality using the mass-balance approach (Plummer and Back, 1980) and stoichiometric "back-reaction" procedures (Garrels and MacKenzie, 1967; Cleaves and others, 1970; Siegel, 1982; Siegel and Pfannkuch, 1984b). The hypothetical models and mass balances will be tested by the isotopic content of carbon in dissolved inorganic carbon species (Wigley and others, 1978) and in solid carbonate minerals identified in the drift.

Equilibrium between solid phases and solution will be determined with the WATEQF computer program (Plummer and others, 1976). Redox will be calculated from redox pairs, including ferric and ferrous iron and sulfate and sulfide, and from dissolved oxygen determined in the field.

This study will be done in close collaboration with M. J. Baedeker of the U.S. Geological Survey in Reston, Virginia, who will be investigating the

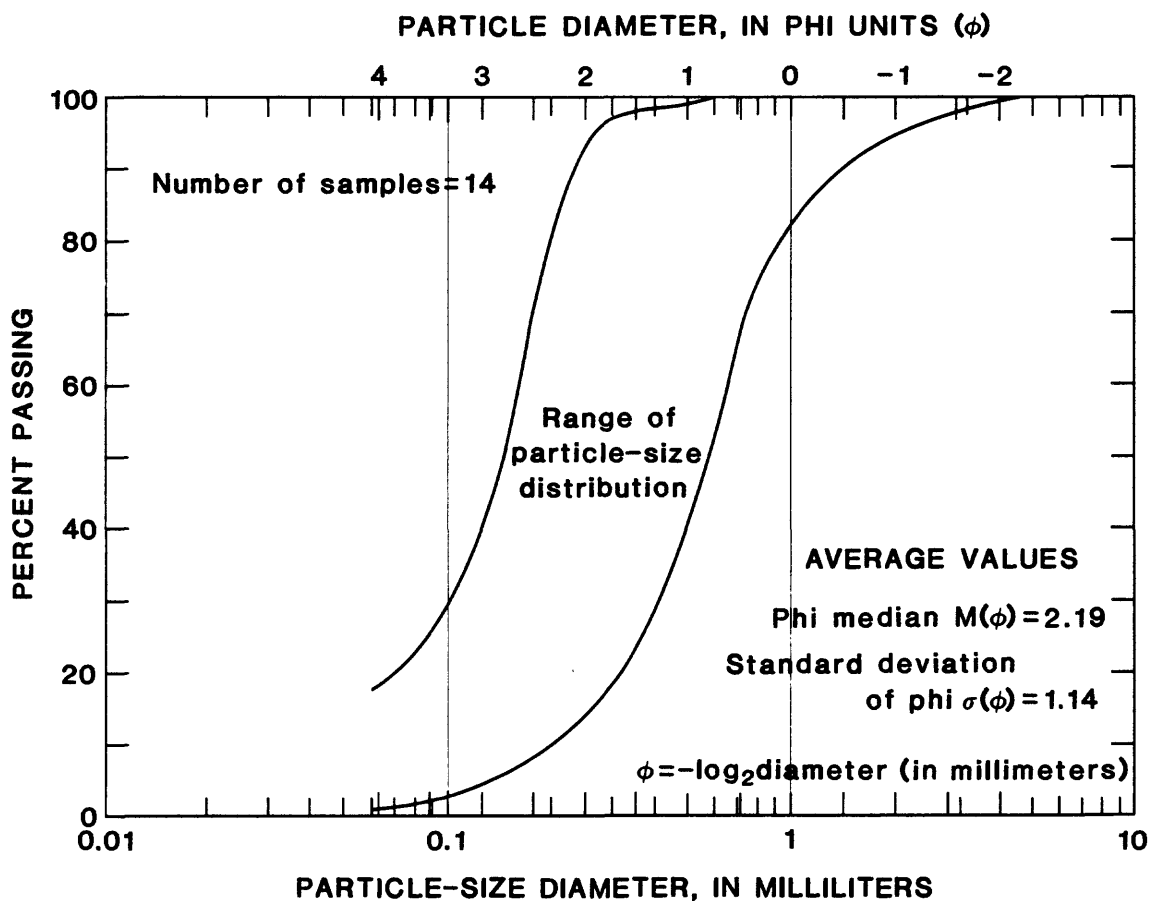
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<sup>1</sup> The use of brand names in this report is for identification only and does not infer endorsement by the U.S. Geological Survey.  
organic geochemistry of unstable constituents at the site. Analysis of ground-

organic geochemistry of unstable constituents at the site. Analysis of ground-water samples for most dissolved inorganic constituents will be done at the U.S. Geological Survey National Laboratory in Atlanta, Georgia. Selected analyses for halogens and other trace constituents, such as vanadium and boron, will be done at Syracuse University or Lafayette College.

#### PRELIMINARY RESULTS

Particle-size analyses of 14 samples of drift taken from cores collected near the oil-spill area show that a large part of the aquifer consists of moderately to poorly sorted medium sand. The average median grain size, determined by the method of moments, is 2.19 phi and the average standard deviation is 1.14. The range of particle-size distributions is shown in figure 29. Less than 10 percent of the drift analyzed is in the silt and clay size fraction.



**Figure 29.--Range of particle-size distributions of glacial drift near Bemidji, Minnesota.**

Hydraulic conductivity of the samples was estimated by the Hazen method from each particle-size distribution using the equation

$$K = Ad_{10}^2$$

where:

K is hydraulic conductivity, in m/s;

A is constant, equal to 0.01; and

$d_{10}$  is the grain size at the 10th percentile of the particle-size distribution.

Hydraulic conductivity ranged from less than  $0.4 \times 10^{-4}$  m/s to  $2.7 \times 10^{-4}$  m/s (table 7) and varied unsystematically with depth, as is common in glacial deposits. Because all values of hydraulic conductivity are within one order of magnitude, the observed differences may be significant, reflecting sedimentological changes, or an artifact of the estimation procedure. Studies of the sedimentological structures in the drift should help to resolve the question.

X-ray diffractograms of selected samples of drift were determined for the silt plus clay particle-size fractions to qualitatively determine the major minerals present (fig.30). Major minerals identified are quartz, calcite, dolomite, and feldspar. No clay minerals were identified, indicating that the clay-size fraction of the drift is probably less than 5 percent by weight. Additional samples of drift will be collected to obtain larger amounts of material for intensive characterization of the fine-grained fractions of the drift.

#### SUMMARY

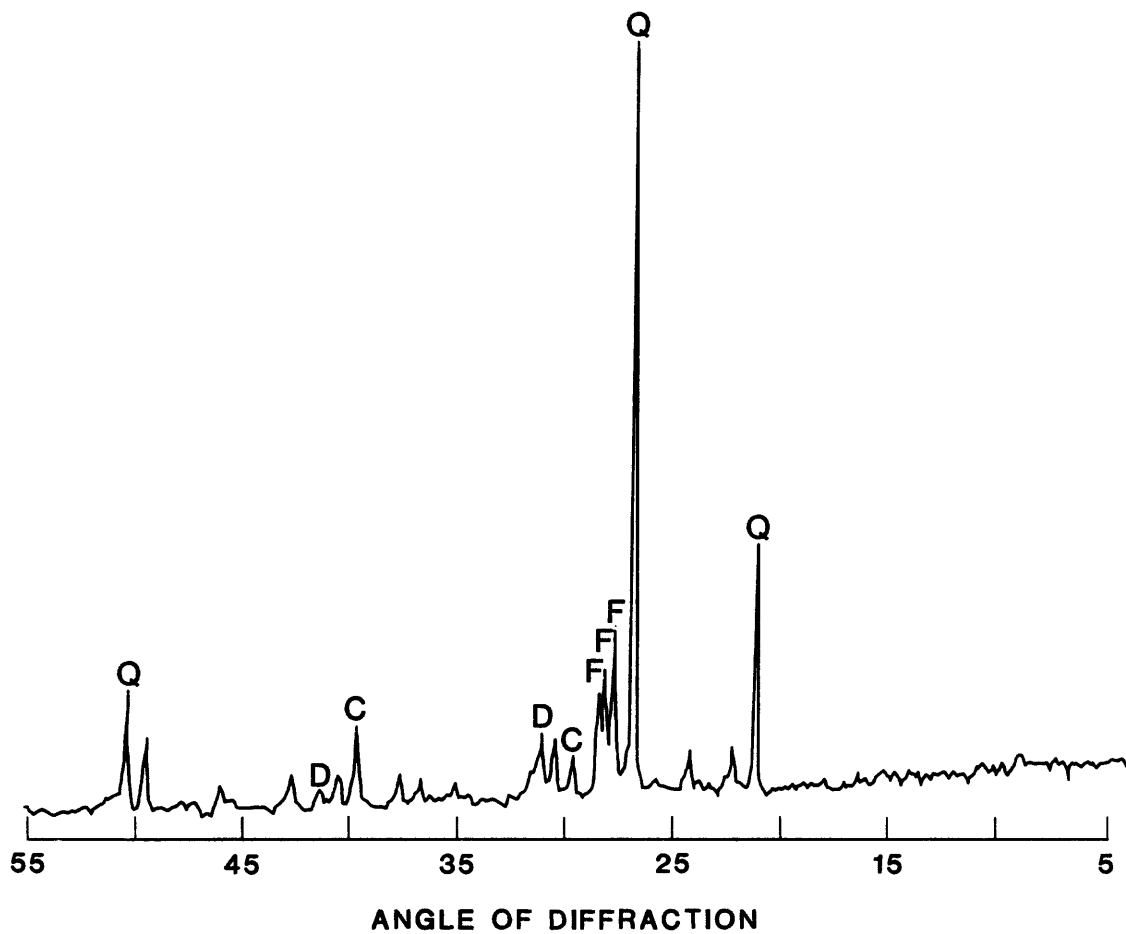
The proposed study of the inorganic chemistry of a ground-water system contaminated by a spill of crude oil near Bemidji, Minnesota, will involve: (1) detailed analysis of chemical partitioning among the major solid phases, (2) textural and mineralogical investigations, and (3) modeling of rock-water interactions in the contaminated and uncontaminated parts of the aquifer. Methods to be used include x-ray diffraction, sedimentary petrography, scanning electron microscopy, chemical analyses of selected minerals, and selected leaching experiments. Particle-size distributions of 14 samples of the glacial drift suggest that much of the aquifer is poorly sorted medium sand. Hydraulic conductivity estimated from grain-size distributions is on the order of  $1 \times 10^{-4}$  m/s. X-ray diffraction of drift samples indicates that the major minerals in the silt-plus-clay fraction are quartz, calcite, dolomite, and feldspar. Identification of clay minerals is incomplete.

Evolution of the inorganic quality of the native and contaminated waters will be evaluated by the mass-balance approach, using the solid-phase information and water-quality analyses. This approach, coupled with environmental-isotopic data on carbon, will indicate the extent to which the petroleum contamination enhances or hinders dissolution of minerals from the aquifer.

**Table 7.—Particle-size distribution and estimated hydraulic  
conductivity of selected drift samples**

[Sat is saturated zone, unsat is unsaturated zone,  $M\phi$  is median phi grain size,  $S\phi$  is average phi standard deviation, and  $D_{10}$  is grain diameter at 10 percent passing interval on cumulative frequency curve]

Sample	Depth (m)	Saturated or unsaturated zone	$M\phi$	$S\phi$	$D_{10}$ (mm)	Hazen's K (m/s)
316-A	7.5-7.6	unsat	1.70 $\phi$	1.43 $\phi$	0.085	$0.7 \times 10^{-4}$
316-B	7.6-7.8	unsat	1.04 $\phi$	1.42 $\phi$	.138	$1.9 \times 10^{-4}$
316-C	14.3	sat	2.40 $\phi$	1.19 $\phi$	.081	$.7 \times 10^{-4}$
317-A	8.4-8.5	unsat	2.30 $\phi$	1.35 $\phi$	.066	$.4 \times 10^{-4}$
317-B	8.5-8.7	unsat/sat	2.37 $\phi$	1.23 $\phi$	.073	$.5 \times 10^{-4}$
317-C	8.7-8.8	unsat/sat	1.83 $\phi$	1.29 $\phi$	.130	$1.7 \times 10^{-4}$
317-D	8.8-9.0	sat	1.76 $\phi$	1.69 $\phi$	.090	$.8 \times 10^{-4}$
318-A	8.8-9.0	unsat	3.03 $\phi$	1.19 $\phi$		$<.4 \times 10^{-4}$
318-B	9.0-9.1	unsat	2.46 $\phi$	1.15 $\phi$	.070	$.5 \times 10^{-4}$
318-C	10.2-10.4	sat	2.91 $\phi$	.68 $\phi$	.088	$.8 \times 10^{-4}$
B304	6.4-6.6	—	2.76 $\phi$	.70 $\phi$	.090	$.8 \times 10^{-4}$
B307	2.7-3.0	—	1.75 $\phi$	.83 $\phi$	.165	$2.7 \times 10^{-4}$
P202	13.4-13.7	—	1.87 $\phi$	.73 $\phi$	.145	$2.1 \times 10^{-4}$
W303	6.9-7.2	—	2.54 $\phi$	1.12 $\phi$	.076	$.6 \times 10^{-4}$



#### EXPLANATION

Q Quartz  
C Calcite  
D Dolomite  
F Feldspar

**Figure 30.--X-ray diffractogram of sample 317-A for less than 0.06 millimeter size fraction drift of glacial drift near Bemidji, Minnesota.**

The approach also will provide information on retention or release of inorganic constituents on or from the solid phase by processes such as sorption, and precipitation, and dissolution.

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## CHAPTER H

### **MICROBIAL RECONNAISSANCE AT THE SITE OF A CRUDE-OIL SPILL:**

#### **PRELIMINARY RESULTS AND PROJECT PLAN**

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#### **ABSTRACT**

Preliminary analysis of microbial populations has been made near the site of a crude-oil spill northwest of Bemidji, Minnesota. Samples of outwash sand were collected from both water saturated and unsaturated zones in an uncontaminated area near the spill. Dilutions were made and spread over the surface of plates of predried Standard Method agar, Bacto-Peptone agar with Tween 80, Basal agar, and Tauson's agar with 1 percent hexadecane or petroleum as sources of carbon and energy for enumeration of total microbial counts and hydrocarbon-degrading bacterial counts. Petroleum-degrading bacteria were also enumerated using three-tube most-probable number (MPN) procedures. A high degree of variability was found between plate counts and MPN estimates. The differences in number are about four to five orders of magnitude. The petroleum degraders were about  $9 \times 10^{-4}$  to  $8 \times 10^{-3}$  percent of the total bacterial counts and the highest percentage of petroleum-degrading bacteria was found in samples that had lowest total bacterial counts. Tentatively, seven to eight bacterial genera were identified: Acinetobacter, Aeromonas, Vibrio, Pseudomonas, Mycobacterium, Micrococcus, and Achromobacter/Alcaligenes. Further research plans described in this paper include isolation of anaerobes, biodegradation kinetics of hydrocarbons, and extraction and analysis of hydrocarbons and degradation products.

#### **INTRODUCTION**

Petroleum spilled in the natural environment is subject to several weathering processes (National Academy of Science, 1975) that change the chemical composition of the petroleum and lead to various hydrocarbon mixtures with properties quite different than the original petroleum. The important biological weathering process is microbial hydrocarbon degradation; the physical-chemical weathering processes include evaporation, dispersion, emulsification and photo-oxidation (Floodgate, 1973).

The addition of hydrocarbons to an ecosystem, as occurs from petroleum spills, will enrich microbial populations that are capable of utilizing the petroleum and capable of utilizing the metabolic products generated by the primary populations of hydrocarbon degraders.

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Some hydrocarbons in petroleum are toxic and/or carcinogenic, and may threaten drinking-water supplies or adversely affect surface-water bodies in discharge zones. The fate of hydrocarbon after a petroleum spill or similar event is, therefore, a matter of some concern.

It is widely accepted that petroleum is decomposed by microbes under aerobic and, to a lesser extent, anaerobic conditions at the expense of oxygen, nitrates, and sulfates, leading to the formation of carbon dioxide, nitrite, nitrogen gas, and hydrogen sulfide. Under oxygen-depleted conditions, a mixed microflora brings about the reduction of significant quantities of sulfate along with the gradual degradation of petroleum. Zobell and Prokop (1966) reported that the sulfate ion is the principal hydrogen-ion acceptor in hydrocarbon biodegradation in anaerobic sediments. Kincannon (1972) indicated that most crude oils can be degraded biologically in the presence of mixed cultures of bacteria.

The most common petroleum-degrading bacteria in aquatic environments are Achromobacter, Pseudomonas, Acinetobacter, Arthrobacter, Micrococcus, Corynebacterium, Vibrio, Brevibacterium, Flavobacterium, and Nocardia. Candida, Sporobolomyces, Cladosporium, and Rhodotorula are the most abundant fungi species. Two nonphotosynthetic algae Prototheca species are capable of degrading hydrocarbons. These microorganisms are widely distributed in oil fields, coastal areas, and soils, particularly in localities subjected to frequent pollution by petroleum or refinery products. Investigation of the distribution of petroleum-utilizing microorganisms, as well as the potential hydrocarbon biodegradation activities of these microbes, are important for assessment of the fate of individual petroleum hydrocarbons in specific ecosystems.

The following hypotheses are being considered at the Bemidji research site: (1) higher microbial populations (especially hydrocarbon-degraders) will be found in the petroleum contaminated site relative to the unpolluted sites nearby; (2) petroleum is subjected to microbial degradation and mineralization in both the unsaturated and saturated zones; (3) dissolution of the petroleum is a biologically mediated process; and (4) the rates of mineralization are dependent on temperature, oxygen, the concentration of nitrate, sulfate, and available mineral nutrients, and the availability of other organic compounds that can be used as carbon and energy sources. For a description of the Bemidji research site, refer to Chapter A of this volume.

The objectives of this study are to: (1) characterize and identify major zones of microbial activity in the subsurface, (2) determine and compare the relative rates of mineralization and dissolution of oil samples taken from different localities and strata, and (3) identify groups of compounds being degraded and produced under aerobic and anaerobic conditions.

#### METHODS OF STUDY

Samples to be used in this investigation will be collected from the following localities: investigation: (1) control samples of uncontaminated outwash sand from both water saturated and unsaturated zones near the petroleum-spill site, (2) original petroleum samples in which no microbial

activity has begun, (3) unsaturated zone above the petroleum, and (4) saturated zone below the petroleum where it has mixed with water and contains organic carbon within a range of 5 to 15 mg/ml.

### Plate Counts

Plate count is the number of colonies that develop after incubation at 6°C on a medium designed to promote growth of microorganisms. Serial dilutions prepared with sediment or ground water were plated out on a Basal agar, Tauson's agar for the enumeration of hydrocarbon or petroleum and Bacto-Peptone agar with 2 percent Tween 80, for the enumeration of hydrocarbon-degrading and lipolytic bacteria, respectively. The plate count of bacteria was recorded as CFU (colony-forming units) per milliliter for water and as CFU per gram (dry weight) for sediment samples.

The sediment samples collected from two different sites and at various depths (925B, 4.0-4.5 ft; 925B, 29.0-29.5 ft; 925B, 33-33.5 ft; 925B, 73.8-74.0 ft; 925B, 78.8-79.0 ft; 310C, 31.0-31.5 ft) were weighed and transferred using sterile equipment. Ten grams (g) of sample were mixed with 95 milliliters (ml) of cold, sterile tap water in a blender at 12,000 revolutions per minute (RPM) for 15 minutes. After blending, the suspension was allowed to settle for 2 minutes, and 10 ml of supernatant liquid were drawn into a pipet and transferred to a 90 ml tap-water dilution blank. Intermediate decimal dilutions in 160 ml milk-dilution bottles were shaken at 350 half-inch excursions per minute for 5 minutes, allowed to settle for 1 minute, and transferred a second time. The second dilution series was prepared by mixing 2.5 g of sediment sample with 23.8 ml of sterile tap water in a 25 x 150 millimeter (mm) test tube. Shaking and decimal dilutions were the same as for the first dilution, except that the shaking time was extended to 15 minutes. Portions of the decimal dilutions (0.1 ml) were spread over the surface of plates of predried Standard Methods Agar and incubated at room temperature under aerobic conditions for 48 hours.

Individual media were prepared as follows:

Tauson's medium with ammonium nitrogen--

(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, 1.0 g; CaSO<sub>4</sub>, 0.5 g; MgSO<sub>4</sub> · 7H<sub>2</sub>O, 0.3 g; FeSO<sub>4</sub> · 7H<sub>2</sub>O, 0.005 g; and distilled H<sub>2</sub>O, 800 ml. A mixture of KH<sub>2</sub>PO<sub>4</sub>, 0.15 g; K<sub>2</sub>HPO<sub>4</sub>, 0.15 g; and distilled H<sub>2</sub>O, 200 ml was autoclaved separately and combined with the Tauson's medium before inoculation. For solid media, add 15 g of Bacto-Agar. A carbon source (1 percent hexadecane or petroleum) must be added prior to inoculation (after inoculation in liquid media). About 0.2 ml of hexadecane or petroleum was used on the agar plates and spread evenly.

Basal medium--

NaCl, 1.0 g; MgSO<sub>4</sub>, 0.5 g; NH<sub>4</sub>NO<sub>3</sub>, 1.0 g; and distilled H<sub>2</sub>O, 1,000 ml. A mixture of 10 percent KH<sub>2</sub>PO<sub>4</sub>, 3 ml; and 10 percent H<sub>2</sub>HPO<sub>4</sub>, 7 ml was autoclaved separately and combined with the basal medium before inoculation. For solid media, add

15 g of Bacto-Agar. A carbon source (1 percent hexadecane or petroleum) must be added prior to inoculation. About 0.2 ml of carbon source was used on the agar plates and spread evenly.

#### Bacto-Peptone medium—

Bacto-Peptone medium, 10 g, is mixed with distilled H<sub>2</sub>O, 1,000 ml. Twenty ml of 2 percent Tween 80 is combined with the autoclaved medium. For solid media, add 15 g of Bacto-Agar.

#### Standard Methods Agar (BBL #11638)—

Peptone, 5.0 g; yeast extract, 2.5 g; glucose, 1.0 g; agar, 15.0 g; and distilled water, 1,000 ml.

### Most-Probable Numbers of Microorganisms

The most-probable numbers (MPN) of microorganisms that can oxidize petroleum and hexadecane were estimated using the three-tube technique and a basal medium. A concentrated solution containing phosphate ion at pH 7.0 and liquid basal medium were autoclaved separately and added to autoclaved basal broth. One-tenth of 1 ml of autoclaved petroleum, or hexadecane, was added to 10 ml of the mixture and represented the sole carbon and energy sources for microbial growth. The inoculated mixture was incubated at 25°C for 10 to 14 days. Growth was detected by pellicle formation at the hydrocarbon-droplet surface and by the turbidity of the water phase in contact with the petroleum or hexadecane.

### Isolation of Anaerobic Bacteria

Sulfate- and iron-reducing bacteria will be isolated using multiple-tube procedures and pre-reduced, anaerobically sterilized media. Denitrifying bacteria will be determined by the multiple-tube technique using citrate-asparagine broth. Other anaerobic bacteria will be characterized by the roll-tube technique using pre-reduced anaerobically sterilized, peptone-yeast-extract glucose agar. Methanogenic bacteria will be characterized by the presence of methane in the head space above the medium.

### Identification of Bacterial Type

After growth, media showing bacterial growth colonies with different morphologies were streaked on Bacto-Peptone agar with Tween 80 Basal agar and Tauson's agar to which 1 percent petroleum had been added and, the cultures were incubated at 28.5°C. The culture plates were examined under a stereomicroscope to characterize growth forms and colony shapes. Gram, spore, and acid-fast stains of each purified bacterium were prepared and examined as soon as the colonies appeared on the agar plates. Biochemical tests and diagnosis of purified cultures were conducted by following principles of biochemical tests in diagnostic microbiology by Blazevic and Ederer (1975) and Bergy's Manual of Determinative Bacteriology (Buchanan and Gibbons, 1974), respectively.

## RESULTS AND DISCUSSION

The results of plate counts of bacteria on Standard Method agar of essentially uncontaminated (control) core samples taken from the Bemidji research site are shown in table 8. Sample location 925B is generally down-gradient from the petroleum spill and sample location 310C is generally upgradient. With the exception of the sample collected from the unsaturated zone at a depth of 29.0-29.5 ft, the bacterial counts are not significantly different in the unsaturated and saturated zones. Plate counts of the shaken samples are higher than the homogenized samples, although no statistical analysis was performed.

Table 9 shows total counts of bacteria grown on Bacto-Peptone agar with the addition of 2 percent Tween 80. It is interesting to note that the counts in colony-forming units are much higher than data given in table 8. This is because a different medium was used. It is important that comparable, standardized methods for enumerating petroleum-degrading microorganisms be used if data from different laboratories are to be compared. Based on total counts of bacteria, there is no difference between samples of two saturated zones (33.0-33.5 ft and 73.8-74.0 ft) (table 9). However, the sample from the unsaturated zone (29.0-29.5 ft) has the highest count; the sample from the saturated zone (78.8-79.0 ft) has the lowest total count. Site number 310C is closer to the oil-spill area, but is located upgradient from the spill and does not show a higher total bacterial count.

The MPN estimates of hexadecane and petroleum utilizers are given in table 10. There is a high degree of variability between plate counts and MPN estimates. The differences in number are about four to five orders of magnitude. The percentage of petroleum degraders was estimated by dividing the most-probable number of petroleum degraders by the total bacterial counts of each sample, and ranged from about 0.0009 to 0.03 percent. Our finding was about two orders of magnitude lower than that reported by Cooney and Summers (1976) who found that 0.1 percent of the total heterotrophic population of bacteria or yeast and fungi could grow on hydrocarbon as the sole carbon source. The highest percentage of petroleum-degrading bacteria was found in samples that had lowest total bacterial counts, that is, samples collected from 78.8 to 79.0 ft at site 925B and from 31.0 to 31.5 ft at site 310C.

Table 11 summarizes the results of biochemical tests conducted on cultures growing on Bacto-Peptone medium. Seven morphologic groups (consisting of either seven or eight genera) are shown. Most of these groups are known to be important hydrocarbon-degrading microorganisms in the natural environment. A single species, petroleum-degrading Pseudomonas sp., was predominant in the population, appearing on the Basal and Tauson's media used in the hydrocarbon-degradation test. Enumeration of hydrocarbon-utilizing microorganisms might be an important technique in assessing the potential for cleanup of petroleum spills through microbial mineralization in the presence of sufficient nutrients, if the populations of hydrocarbon-degrading microbes are related to the concentration of petroleum in the subsurface. More isolations and

**Table 8.—Plate counts of bacteria on Standard Methods Agar**

[Values for plate counts are given in colony-forming units per milliliter, CFU/ml]

Sample location	Depth (ft)	Plate counts (cfu/ml)	
		Homogenized	Shaken
925 B	4.0-4.5*	$1.0 \times 10^5$	$1.5 \times 10^5$
925 B	29.0-29.5*	$6.0 \times 10^3$	$2.6 \times 10^4$
925 B	33.0-33.5**	$1.0 \times 10^5$	$2.0 \times 10^5$
310 C	31.0-31.5**	$1.0 \times 10^5$	$2.0 \times 10^5$

\* Above the water table.

\*\* Below the water table.

Table 9.—Total counts\* of bacteria on Bacto-Peptone agar with 2 percent Tween 80

[Values for total counts are given in hundred thousand colony-forming units per milliliter, CFU x 10<sup>5</sup>/ml]

Sample location	Depth (ft)	CFU† x 10 <sup>5</sup> /ml		
		Mean	Standard Deviation	Range
925 B	4.0-4.5	126.3 B	18.9	110-147
925 B	29.0-29.5	169.0 A	12.3	155-178
925 B	33.0-33.5	103.0 C	13.1	88-112
925 B	73.8-74.0	101.7 C	12.1	89-113
925 B	78.8-79.0	15.6 E	1.55	140-171**
310 C	31.0-31.5	57.3 D	7.8	51-66

\* Total counts of bacteria were conducted by shaking process.

\*\* Plate counts of sample collected from this depth (78.8-79.0 ft) were done at 10<sup>-4</sup> dilution.

† Values are the mean of three replicates. Different letters following the mean values of each depth are different at 5-percent significance level according to Duncan's Multiple Range test.

Table 10.—Growth of microorganisms on hexadecane and petroleum using the MPN technique

Sample location	Depth (ft)	MPN of hydrocarbon utilizer grown on Basal Broth* (number/ml)		
		Hexadecane	Percent of total population	Petroleum Percent of total population
925 B	4.0-4.5	150 C	$1.19 \times 10^3$	150 D $1.19 \times 10^{-3}$
925 B	29.0-29.5	250 B	$1.48 \times 10^{-3}$	300 B $1.78 \times 10^{-3}$
925 B	33.0-33.5	150 C	$1.46 \times 10^{-3}$	150 D $1.46 \times 10^{-3}$
925 B	73.8-74.0	90 D	$8.82 \times 10^{-4}$	250 C $2.45 \times 10^{-3}$
925 B	78.8-79.0	40 E	$2.56 \times 10^{-3}$	90 E $5.77 \times 10^{-3}$
310 C	31.0-31.5	450 A	$7.85 \times 10^{-3}$	1500 A $2.62 \times 10^{-2}$

\* Numbers are the means of three replicates, same letter following the mean value of hexadecane and petroleum degrader at different depth is not different at 5 percent significance level according to Duncan's Multiple Range test.

Table 11.—Characteristics of bacteria isolated from cultures growing on Bacto-Peptone medium

[+, positive test result; -, negative test result; N, not tested]

Isolate number	Tentative Genus or Family	Pigment Formation <sup>1</sup>	Gram Stain	Acid-Fast Stain	Rod	Catalase	Oxidase	Motile	Methyl Red	Voges Proskauer	Indole Production	Gas-Glucose	Fermented-Glucose	Oxidized-Glucose	NO <sub>3</sub> -Reduced	NO <sub>2</sub> -Reduced	Casein Hydrolyzed	Starch Hydrolyzed	H <sub>2</sub> S Produced	Urea Decomposed
1.	<u>Acinetobacter</u>	-	-	-	+	+	-	-	-	-	-	+	-	-	-	-	-	N	-	-
2.	<u>Aeromonas</u>	-	-	-	+	+	+	+	-	-	-	+	+	+	-	-	-	+	-	-
3.	<u>Vibrio</u>	Y	-	-	+	+	+	+	-	+	-	-	+	+	+	-	-	N	-	-
4.	<u>Pseudomonas</u>	FL	-	-	+	+	+	+	-	-	-	-	-	-	+	-	-	-	N	-
5.	<u>Mycobacterium</u>	Y,O	+	+	+	N	N	-	-	-	-	-	-	-	+	-	N	N	N	+
6.	<u>Micrococcus</u>	YBR	+	-	-	+	-	-	-	-	-	N	N	+	N	N	N	N	N	N
7.	<u>Achromobacter</u> / <u>Alcaligenes</u>	-	-	-	+	+	+	+	-	-	N	N	-	+	-	-	-	+	N	N

<sup>1</sup> Y, yellow; FL, fluorescent; Y,O, yellow to orange; YBR, yellow brown.

characterizations of microorganisms (including fungi and yeasts) will be conducted on samples from the contaminated zone. The study of the microbial-degradation kinetics of petroleum will be initiated in our laboratory using water and sediment samples that have mixed hydrocarbon degraders collected from the spill site. The experimental results are expected to enhance our understanding of naturally occurring processes as well as of stimulated biodegradation of petroleum.

#### BIODEGRADATION KINETICS OF HYDROCARBONS

The rate of oxygen uptake will be determined in sediment suspension or in water-oil samples in 300-ml BOD bottles. Dissolved oxygen and redox potential (Eh) will be assayed periodically using an oxygen electrode and redox potential electrode, respectively. Oxygen-uptake studies also will be done by adding nitrogen (as  $\text{KNO}_3$ ) and/or phosphorus (as  $\text{KH}_2\text{PO}_4$ ) from sterile, concentrated stock solution (pH 7.0) to a control water sample that was collected from the control site and has been mixed with a known quantity of petroleum (or hexadecane or naphthalene) prior to incubation in the dark in the laboratory.

The rate of hydrocarbon mineralization will be determined by incubating 60 ml of water/petroleum (or petroleum and water mixture), or 50 g of sediment that contain petroleum in sterile 500 ml wide-mouth bottles for a period of 5 months. Carbon dioxide evolution will be trapped with 10 ml of 0.5N KOH solution and assayed at different time intervals. The method will follow Chang and Broadbent (1981).

Microbial oxidation of hydrocarbon will also be conducted by using  $^{14}\text{C}$ -labeled hexadecane mixed with water-petroleum or sediment suspension under various controlled concentrations of dissolved oxygen. Mineral nutrients will be added and the mixture will be incubated in the dark for a period of 2 weeks, 5 weeks, 2 months, 4 months, and 5 months. The  $^{14}\text{CO}_2$  will be assayed at the end of each incubation period with a Beckman<sup>1</sup> Liquid Scintillation Counter. The procedures will follow Chang and Alexander (1983) and Harrison and others (1971).

Samples of fresh sediment suspension, water/petroleum mixture and incubated mixtures will be extracted for hydrocarbons and their degradation products by shaking sequentially twice with 50 ml ethyl ether and once with methylene chloride. The extracts will be separated into fractions using silica gel column chromatography. The alkane fraction will be eluted from the column with 20 ml pentane and 5 ml 20 percent (v/v) methylene chloride in pentane. The aromatic fraction will be eluted with 45 ml 40 percent (v/v) methylene chloride in pentane. After elution, each fraction will be reduced in volume to approximately 10 ml at 35°C and transferred quantitatively to clean glass vials. The alkane fraction will be analyzed using a Perkin-Elmer sigma 3B gas chromatograph equipped with a flame ionization detector. The aromatic fraction will be analyzed by gas chromatography with mass spectrometry operated in the selected-ion monitoring mode. Detailed methodology of hydrocarbon extraction and analysis will follow Haines and Atlas (1982).

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<sup>1</sup> Use of brand names in this report is for identification only and does not imply endorsement by the U.S. Geological Survey.

## SUMMARY AND CONCLUSIONS

The petroleum-spill site near Bemidji, Minnesota, contains several important, indigenous genera of bacteria that can degrade hydrocarbons found in petroleum. Among seven (or eight) genera of bacteria, pseudomonas appears to be the most abundant species found in the control samples. There was a high degree of variability found between MPN procedures and plate-count methods. The most-probable number estimates of hydrocarbon utilizers are four to five orders of magnitude lower than the total plate counts.

The mineralization of crude petroleum will be determined by rates of oxygen uptake, carbon dioxide evolution, and  $^{14}\text{C}$  tracing techniques at various incubation periods. Biodegradation products, under different incubation conditions, will be identified at the end of each incubation.

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