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Test Results of Surfactant Enhanced Gasoline Recovery In A Large-Scale Model Aquifer

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FORWARD

The work described in this report was performed at Texas Research Institute, Inc. (TRI), Austin, Texas. The project director was J. Scott Thornton. Principal investigators were Wilford L. Wootan, Jr. (Project Scientist) and Tamara Voynick.

TRI gratefully acknowledges the partial support of this work provided by the American Petroleum Institute (API). Technical guidance was furnished by the Groundwater Committee Technical Task Force.

The statements and conclusions contained in this report regarding the effectiveness of surfactant treatment(s) in mobilizing spilled gasoline for soil/groundwater reclamation are those of the authors and may not represent those of API or of the Task Force members.

EXECUTIVE SUMMARY

The objective of this project was to test whether the use of surface active agents (surfactants) would enhance removal or recovery of gasoline from a contaminated aquaifer. The effects of surfactants used to mobilize spilled gasoline entrained in the capillary fringe of a modeled aquifer were assessed. The surfactant employed was a 2% solution of Richonate YLA, with 2% Hyonic PE-90 added to enhance flow rate.

A 3m x 3m x 1.2m deep (10ft x 10ft x 4ft) sand-filled concrete tank with a nominal 0.3m (1ft) deep, 3% gradient water table was used as model aquifer. The tank interior was temperature controlled and was instrumented for observation of fluid distribution and measurement of fluid levels and flows. Gasoline was metered into the sand volume just above the capillary fringe of the aquifer. The rate of gasoline removal was monitored by collecting raw gasoline from a simulated producing well and by extraction of dissolved gasoline from samples of the produced effluent. A carbon disulfide (CS_2) extraction technique was employed. Calculation of residual gasoline based on core sampling of the sand volume completed mass accountability.

Three surfactant application techniques were tested: a single application by percolation through the sand volume, a multiple (daily) application by percolation, and a multiple (daily) application by direct injection into the water table. The multiple application techniques proved to be the most effective for removing the spilled contaminants. Based on the amount of gasoline in the tank at the beginning of the surfactant application(s), the percentages of gasoline removed associated with each technique were 6, 76, and 83, respectively.

Ancillary observations performed throughout these tests underscored the uncertainty in predicting fluid distribution and fluid flow in even a simply structured soil (e.g., packed sand).

Recommendations are made for further study of surfactants and surfactant application techniques and of fluid flow behavior in model environments before proceeding to full-scale field tests.

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1.0 INTRODUCTION

Gasoline that escapes from a surface or buried container will permeate the soil downwardly and will diffuse laterally. The extent of lateral diffusion relative to downward travel will be determined principally by the permeability of the soil. In the absence of shelf rock or clay, the limit of downward movement will be the upper surface of the aquifer, which presents a virtually impenetrable barrier to the gasoline. When the gasoline percolates to the aquifer, it then spreads horizontally to form a buoyant layer, or lens, on the water surface. The nature and extent of this lens will be determined by the topography and permeability of the aquifer boundary, by the movement of the ground water, and by complex surface interactions among soil, water, and gasoline.

Gasoline is an obvious contaminant of ground water and its spread may lead to underground seepage into open water containments and potential entry of hazardous fluids and fumes into storm sewers, basements, and underground utilities, often with disastrous results.

Gasoline that permeates the pore structure of the aquifer boundary will be dispersed into droplets whose size (or size range) is determined by the interfacial tension between the gasoline and the ground water and by the capillary dimensions of the pore structure. Capillary forces will act to retain these droplets within the soil pores. Some components of the contaminant will adsorb on surfaces within the aquifer fringe and in the overlying unsaturated soil. The result is a zone of gasoline contamination moving along the surface of the water table at a rate slower than the water movement, plus a relatively small volume of gasoline contaminated soil located beneath the spill site. Water, e.g., rain, that enters the soil over the spill site will percolate through this region to leach gasoline into the water table.

Part of the gasoline spilled to the aquifer can be recovered in raw form at a drawdown well or an intercepting trench. However, a significant portion of the spilled gasoline volume will remain entrapped in the pore structure of the aquifer surface in the form of droplets immobilized by interfacial and capillary forces. Recovery of this entrapped volume of contaminant requires that it be mobilized. This can be accomplished by 1) increasing the driving force, e.g., by flooding with water to increase the hydrostatic head, 2) by forcing air to flow through the soil layer to increase the rate of droplet vaporization while in the pores, or 3) by reducing the surficial forces retaining the droplets, thereby allowing them to flow under the existing driving forces and/or to dissolve. It is the last approach to enhancing contaminant mobility that was addressed in the work reported here.

Texas Research Institute (TRI) identified surface active agents (surfactants) that enhanced the removal of gasoline entrapped in the pore framework of simple soils (packed sands), and that would not themselves permanently contaminate an aquifer, and assessed their utility in recovering the entrapped gasoline in a large-scale physical model experiment. Three surfactant application techniques were evaluated: a single dose that percolated through the spill site to the water table, a multiple (daily) dosage that percolated through the spill site, and multiple (daily) injections directly into the water table below the spill site. In a fourth test, the control, water only was percolated through the spill site. The effectiveness of each technique for recovering the spilled gasoline was evaluated singly and by comparison to the other techniques and to the control.

2.0 EXPERIMENTAL FACILITY

The TRI model aquifer facility is diagrammed in Figs. 1 and 2. It is a steel-reinforced concrete tank measuring 6.1m x 3m x 1.2m deep (20ft x 10ft x 4ft) inside. For the present work the tank was divided by a steel partition to form two 3m x 3m x 1.2m (10ft x 10ft x 10ft) tanks to allow parallel testing of different procedures.

The soil fill of each tank was packed, washed river sand, designated "finish" sand by the aggregate supplier. The four tests--three surfactant application techniques plus water application only--required two fillings of each tank. The characteristics of the sands used in the two fillings differed slightly in grain size distribution and, therefore, porosity and permeability. The sands are characterized below. (See also Appendix C.)

Each tank was equipped and instrumented as follows (see Figs. 1 and 2). A water input pipe for establishing and maintaining the water table was located along the centerline near the steel partition. A 30.5 cm (12 in.) high standpipe/recovery well was located along the centerline adjacent to the opposite (end) wall of the tank. A perforated tube grid for simulating rainfall was positioned just above the top of the sand pack. The sides of the tank and the upper margin of the rainmaker grid were striped with copper tubing for circulating coolant water to maintain tank temperature at nominal 13°C(55°F). Seven observation wells made from 3.2 cm (1.25 in.) i.d. PVC pipe slotted to 61 cm (24 in.) height above the tank floor were positioned as diagrammed in Fig. 1. Four large volume vapor wells made from 10 cm (4 in.) i.d. PVC pipe with 100 mesh screen on bottom were positioned as shown in Fig. 1. Thermocouples were placed at three depths--15 cm (6 in.), 61 cm (24 in.), and in the water table--near the steel divider and the end wall and near the center of the tank to

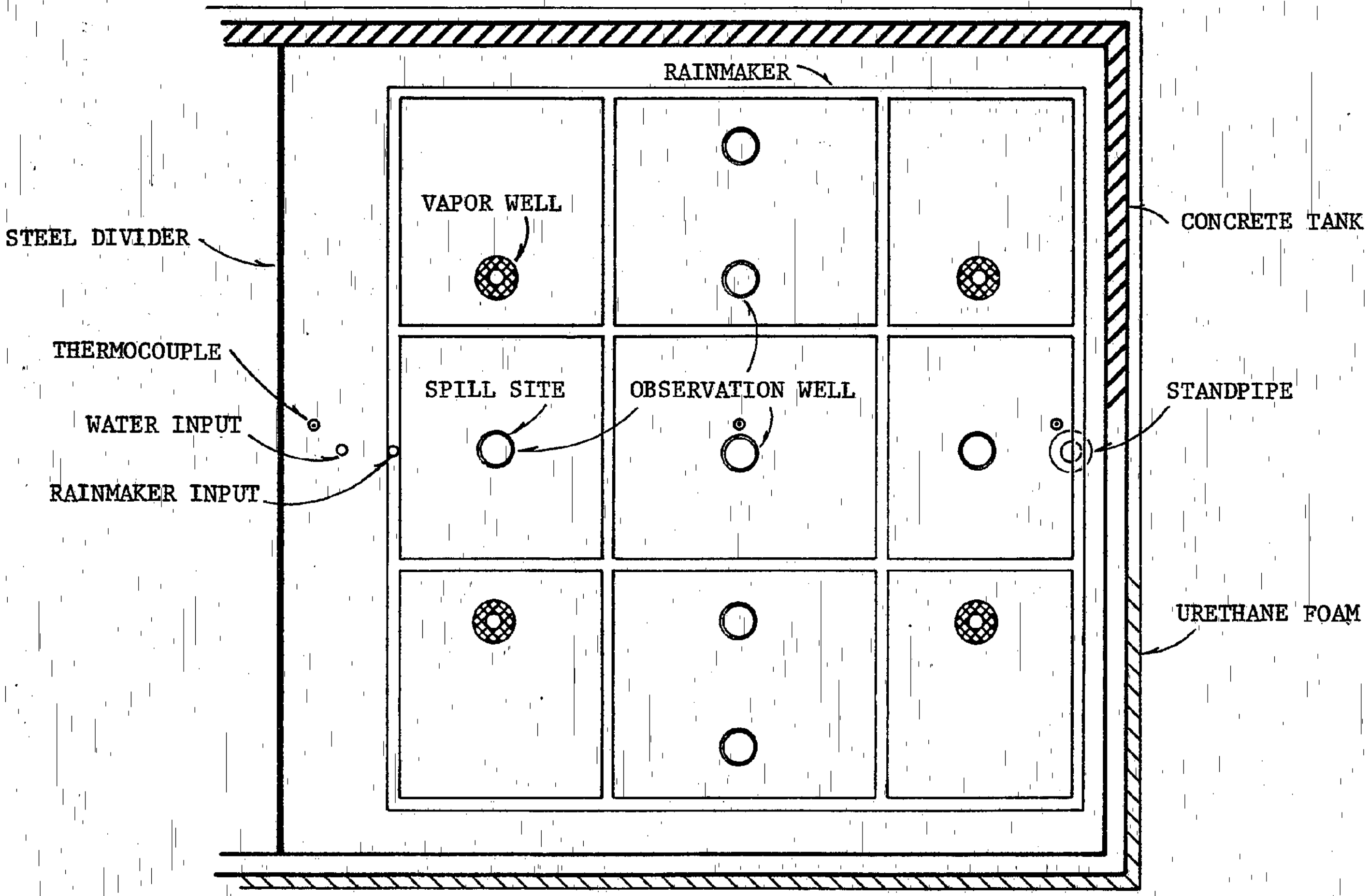

Figure 1

TRI Soil/Aquifer Model Facility

Plan View

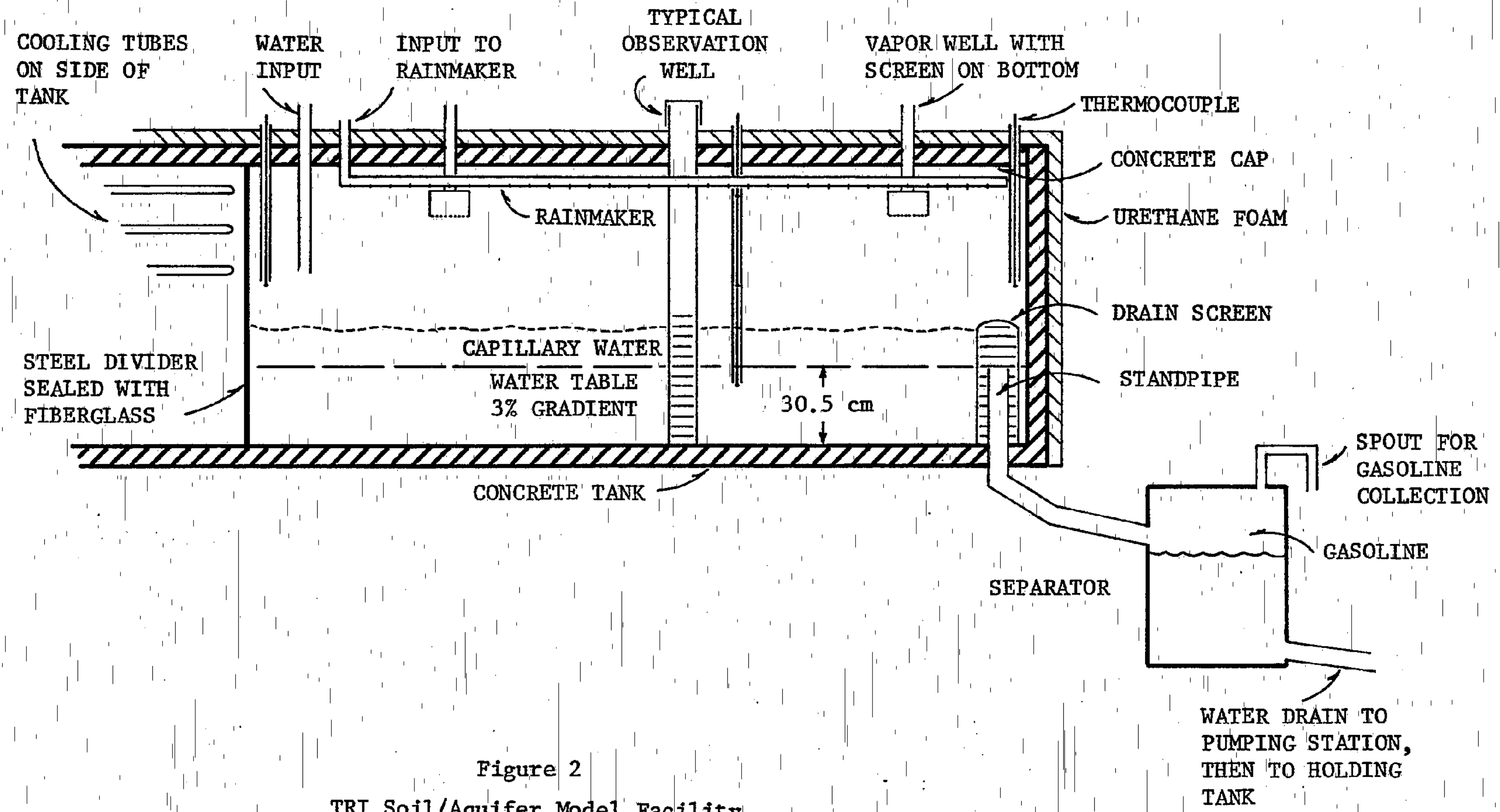

Figure 2

TRI Soil/Aquifer Model Facility

Side View

monitor the temperature profile of the model aquifer; an additional thermocouple was located externally to monitor ambient temperature.

A plywood barrier was laid over the cooling coils above the sand pack and a nominal 5 cm (2 in.) thick concrete cap was poured in place to reduce evaporative losses from the tank and, by acting as an oxygen barrier, to reduce bacterial activity in the model aquifer. The entire structure was then spray coated with polyurethane foam to a thickness of 5 cm (2 in.) for insulation and further sealing. Photographs of the surface of a filled tank before the concrete cap was poured and after it was spray coated with foam are included as Appendix A.

The water table was set at 30.5 cm (12 in.) above the tank floor. Untreated City of Austin tap water--pH 9.7 to 10.0--was used. The input flow was adjusted to establish and maintain a nominal 3% water table gradient.

Effluent was passed through a separator for removal of raw gasoline. The effluent water was sampled for analysis and the remainder was pumped to a holding tank for subsequent disposal (transport to a sewage treatment facility).

The grain sizes of the sand used in the first pack are represented by the following sieve analysis results.

Mesh Size	Wt % Passing
5	99.9
10	96.8
20	81.0
35	51.1
50	22.5
100	4.8

The porosity of this sand was 33%. Its permeability was 19 darcies. Capillary height was approximately 15 cm (6 in.). Surfactant adsorption studies indicated that 20-30% of the surfactant in one pore volume of solution was retained by the sand.

The grain sizes of the sand used in the second pack are represented by the following sieve analysis results.

Mesh Size	Wt % Passing
5	100
10	98.4
20	81.5
35	44.2
50	14.9
100	2.8

That is, the median grain size of this sand was slightly larger than that of the earlier sand. Its porosity was 34%, an insignificant difference from the earlier sand, but its permeability was 37 darcies, a two-fold increase. Capillary height was approximately 13 cm (5 in.). Surfactant adsorption studies on this sand indicated that about 20% of the surfactant was removed from solution by the sand.

3.0 EXPERIMENTAL PROCEDURE

Four experiments were conducted using the model aquifer facility described above. Three of these were to assess the effectiveness of different surfactant application techniques in mobilizing soil and gasoline trapped in ground water for removal and/or recovery. The fourth was a comparison or control test to assess recovery in the absence of mobilizing agents.

The surfactant employed was a 2% solution of Richonate YLA (Richardson), with 2% Hyonic PE-90 (Diamond Shamrock) added to enhance flow rate. Earlier work at TRI* has shown that the anionic Richonate YLA was effective in displacing gasoline from a sand pore framework by reducing the gasoline-water interfacial tension. However, used alone it formed a viscous emulsion with an intolerably low flow rate. The addition of the nonionic Hyonic PE-90 increased the flow rate without decreasing the effectiveness of the YLA.

The original test plan specified that during the first phase of the experimental program, one of the surfactant application techniques would be compared to the control. Then, in the following phase, this application technique would be repeated for comparison with a second application technique. However, the results from the Phase I assessment revealed a need to modify the testing program. Therefore, during Phase II, two additional surfactant application techniques were assessed. (See below.)

The Phase I tests consisted of the control--no surfactant applied--and a single application of surfactant by percolation through the sand. The experimental procedure for these tests was as follows.

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*Texas Research Institute, Inc., "Underground Movement of Gasoline on Groundwater and Enhanced Recovery by Surfactants," Final Report (September 14, 1979) submitted to the American Petroleum Institute.

1. On Day 1 a nominal 3% gradient of the water table was established, and
2. 75.7 liters (20 gal) of gasoline (unleaded, 87 octane) were "spilled" into each tank at the high end of the water table through the observation well identified in Fig. 1. The gasoline was siphoned from 19 liter (5 gal) cans through a small tube over a 4 hour period.
3. On Day 18, 94.6 liters (25 gal) of surfactant solution (water in the control) were trickled onto the soil surface via the rainmaker grid.
4. On the following two days, Days 19 and 20, 208 liters (55 gal) of water per day were added through the rainmaker to wash any pore-space-entrapped surfactant down to the gasoline contaminated soil above the water table. Equal volumes of water were similarly applied in the control test.
5. On Day 26 a third washdown, not originally scheduled, with 208 liters of water was applied to determine whether any additional surfactant could be removed from the soil. Again, a similar volume of water was percolated through the control soil.
6. All measurements were terminated on Day 30.
7. Core samples of the sand pack in each tank were taken on Day 32 for use in determining residual gasoline contents.

The Phase II tests consisted of multiple (daily) applications of surfactant, without washdown, in one case via the rainmaker to percolate through the contaminated soil, in the other case by direct injection into the water table via an observation well. The experimental procedure for these tests was as follows.

1. The water table gradient, nominal 3%, was established on Day 1, and,
2. 75.7 liters of gasoline were spilled into each tank via the observation well identified in Fig. 1. Again, the gasoline was siphoned from 19 liter (5 gal) cans through a small tube but this time over a 6 hour period.
3. Beginning on Day 17 and continuing through Day 29, 94.6 liters of surfactant solution per day were, in one tank, trickled onto the soil surface via the rainmaker to percolate through the gasoline contaminated soil to the water table, and in the other tank were injected directly into the water table via an observation well.
4. Measurements of gasoline recovery and/or removal were terminated on Day 30.
5. Core samples of the sand pack in each tank were taken on Day 31 for use in determining the residual gasoline contents.

The measurements and analyses described below were performed during each Phase of the experimental program.

1. The volume of raw (liquid) gasoline in the separator (see Fig. 2) was measured twice daily. Samples of the effluent water were collected at the same time for later analysis for dissolved hydrocarbon content. The raw gasoline was analyzed by gas chromotography (GC) to evaluate the percentages of heavy and light fractions. Immediately upon collection of effluent a 20 ml sample was extracted with 2 ml of CS_2 in a separatory funnel; extracts were stored at -10°C and analyzed weekly for dissolved hydrocarbon content.

Analysis was by GC using a 6m FFAP column and a flame ionization detector (2 1 injections; temperature program from 75°C to 200°C at 49°C/min after 2 min initial hold). The CS_2 peak was arbitrarily chosen as the demarcation between light and heavy fractions. The selection of the CS_2 extraction technique vis-a-vis other techniques was predicated on development work at TRI that demonstrated its effectiveness in these applications.

2. Samples of the effluent were collected daily but were frozen for weekly analysis of surfactant content. Analysis involved complexing the anionic Richonate YLA with methylene blue, followed by colorimetric determination (see Appendix C).
3. Gasoline and water levels in the observation wells were determined twice daily using a dipstick. Water level was measured by detecting electrical conductivity; gasoline depth was measured using a wettable surface.
4. CO_2 in the sand pore spaces was monitored on a daily schedule. Samples were drawn from one of the four vapor wells on a rotating basis and passed through a dry ice/ethanol cold trap and a charcoal tube to remove hydrocarbon vapors. Evaluation was by GC using a 2m Porapak Q Column with a reducing catalyst (conversion of CO_2 to CH_4) and a flame ionization detector.
5. CO_2 and O_2 contents in the input water and effluent were determined twice daily. CO_2 was evaluated by ion selective electrode (Orion Model 95-02). O_2 was measured by use of a membrane electrode (Yellow Springs Instruments Model 5331).
6. The pHs of the input and effluent waters were measured daily using a research grade combination pH electrode.

7. Model aquifer and ambient temperatures were recorded continuously on a 24 channel strip chart recorder.
8. At the end of each phase, a number of core samples from each tank were removed and the residual gasoline was extracted with 1.5 liters of CS_2. A 5.7 cm (2.25 in.) diam core from the sand surface to the piezometric level was removed. Extraction took place in one gallon glass vessels with intermittent agitation. Quantification of gasoline content was by GC.
9. The porosity, permeability, capillary height, particle size distribution, and surfactant adsorption of the sand used in each phase were determined using the techniques described in Appendix C.

4.0 RESULTS AND DISCUSSION

4.1 Phase 1

Figure 3 displays gasoline recovery and removal during the two tests constituting Phase I of the experimental program: the no-surfactant control and a single application of surfactant followed by sequential washdowns (see Sec. 3.0). Each plot is identified in the figure; the control test data in each plot are shown by the solid curve. The vertical line labelled "surfactant" (Day 18) identifies the day on which surfactant was applied in the surfactant application test and on which water was first applied in the control test.

Daily totals of raw gasoline collected from the separators are displayed in the lower plot; the ordinate is in liters. The total volume of raw gasoline recovered in the control test was 23.4 liters, or 30.9% of the spilled volume. The total volume of raw gasoline recovered in the surfactant application test was 15.3 liters, or 20.2% of that spilled. The difference is presumed to be due to differences in the flow characteristics of the sand packs in the two test tanks.

The application and subsequent percolation of surfactant through the soil/aquifer is represented by the plot second from the bottom in Fig. 3, labeled "Dissolved Surfactant in Effluent;" the ordinate is in ppm (see Appendix C for details of the analysis). The volumes of dissolved gasoline in the daily samples of the effluents are shown in the third plot up, labeled "Dissolved Gasoline in Effluent." Following the application of surfactant and subsequent washdowns, there is a noticeable peak in the data (curve) for this test; also, the amounts of dissolved gasoline are henceforth greater than in the control. The total volumes of dissolved gasoline in the control and in the surfactant tests, respectively, were

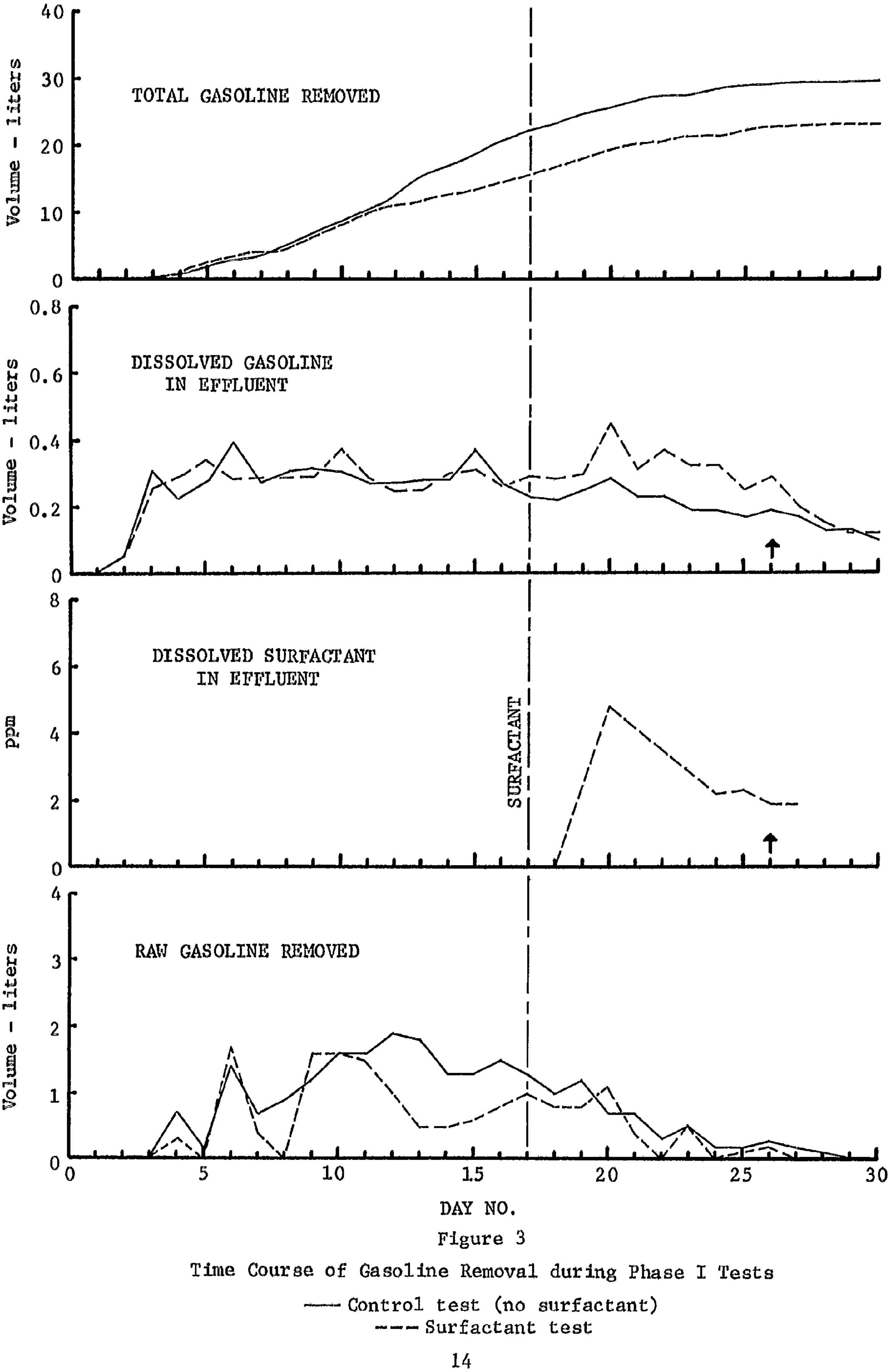

Figure 3

Time Course of Gasoline Removal during Phase I Tests

—— Control test (no surfactant)
– – – Surfactant test

6.8 liters, or 9.0% of the volume spilled, and 7.8 liters, or 10.3%. Analogous values for the two tests before (Days 1-17) and after (Days 18-30) the surfactant application are, respectively: 4.35 liters, 5.75%, for the control, 4.36 liters, 5.76%, for the surfactant test; and 2.49 liters, 3.3%, for the control, 3.47 liters, 4.58%, for the surfactant test. The latter difference is significant at a 0.05 level as determined by the t-Test for uncorrelated means.

Two possible explanations for the unexpectedly small increase in gasoline removal following application of the surfactant were postulated: 1) that the volume of surfactant used was insufficient to alter the mobility of the entrapped gasoline effectively; or 2) that further washdown of the surfactant to the water table was needed. The latter hypothesis was examined by implementing a third washdown on Day 26 (arrows, Fig. 3) with an additional (unscheduled) 208 liters of water via the rainmaker grid in each tank. Evaluation of dissolved gasoline in the effluents showed small increases in both the control and surfactant tests, indicating that this was due to the additional flow through the contaminated area and not to additional surfactant being washed down. Also, the additional washdown had no significant effect on the level of the surfactant in its effluent, indicating that most of the surfactant had already been washed down.

Since the third surfactant washdown had only a minimal effect on mobilizing gasoline, the low gasoline yield was assumed to be due to an insufficient quantity of surfactant rather than a failure to deliver the surfactant to the contaminated zone. For this reason, the experiments in Phase II were modified to include additional quantities of surfactant.

The upper plot in Fig. 3 shows cumulative curves of total gasoline removed--raw gasoline collected from the separators and that dissolved in the effluents--during each test. The total volume removed from the control tank was 30.2 liters, or 39.1% of the total volume spilled; that from the surfactant application tank was 23.0 liters, or 30.8%. The divergence of the two curves beginning on about Day 12 is unexplained.

The daily volumes of gasoline recovered from the separators plus that dissolved in the effluents are plotted in Fig. 4. This figure illustrates the ineffectiveness of the single application of surfactant.

Figure 5 displays the daily water levels and the floating gasoline levels measured in the seven observation wells of each tank (see Figs. 1 and 2). The depth of floating gasoline is added to the water depth so that the top line of each graph represents the total depth of liquid in each well. The measurements for the control test are shown in the lower portion of the figure; those for the surfactant test in the upper portion. The location of the standpipe/recovery well is indicated for referencing these data to the plan view shown in Fig. 1. The arrow in each of the upper profiles indicates the day the surfactant was applied.

The similarity between the profiles in each test indicates that the spilled gasoline spread uniformly across the water table in each tank. Note that shortly after the spill, gasoline flowing along the surface of the capillary fringe of the water table enters the observation well and falls to the piezometric surface, where it begins to displace the water column in the wells. Since the gasoline does not easily flow into the lower portion of the capillary zone, water is forced out of the bottom of the well and back into the aquifer. As gasoline is removed from the tank, the mass loading on the water column in each well diminishes and water seeps

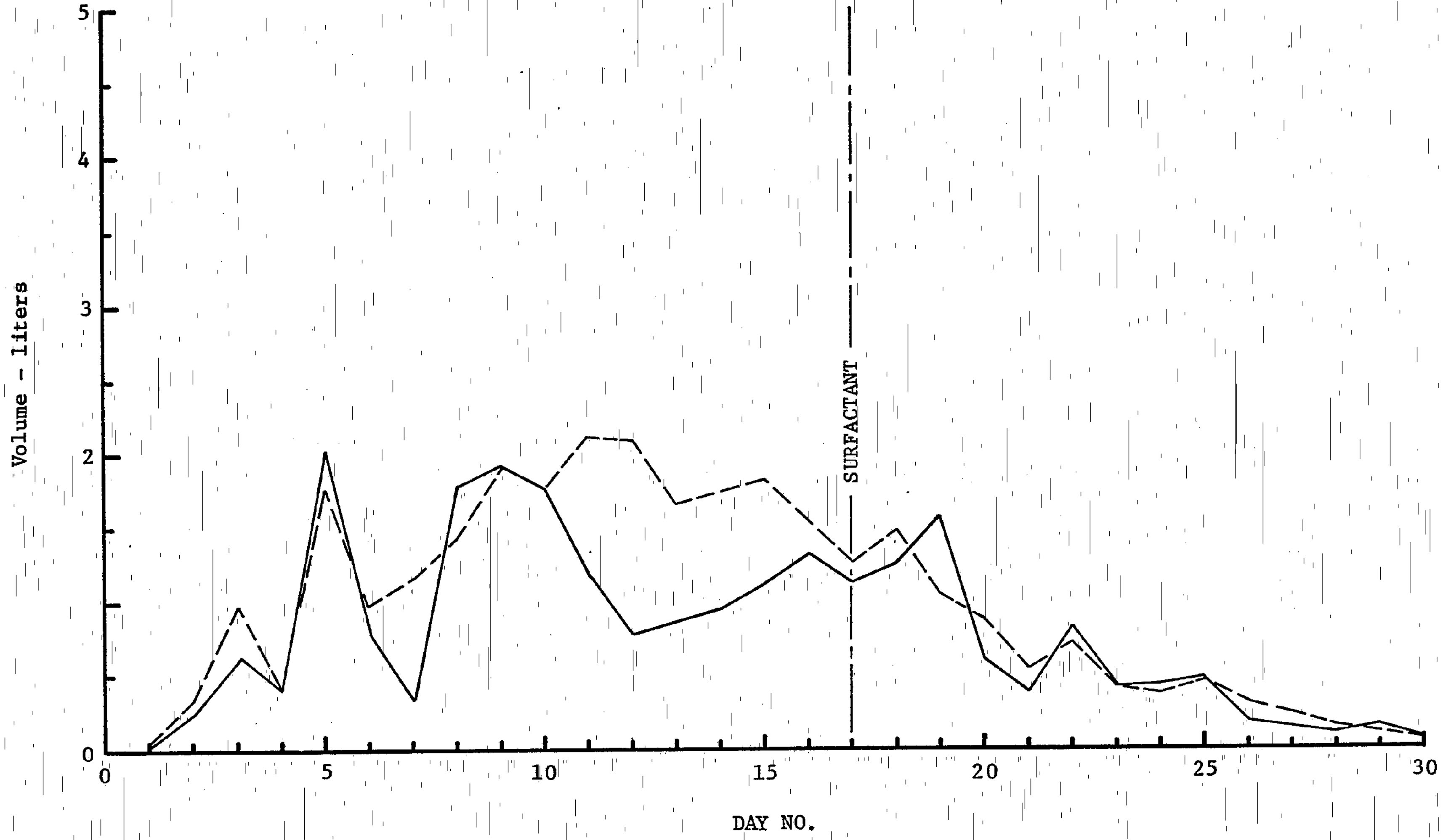

Figure 4

Daily Volumes of Gasoline Removed from Separators and Effluents
Phase I

——— Single percolation of surfactant
— — — Control

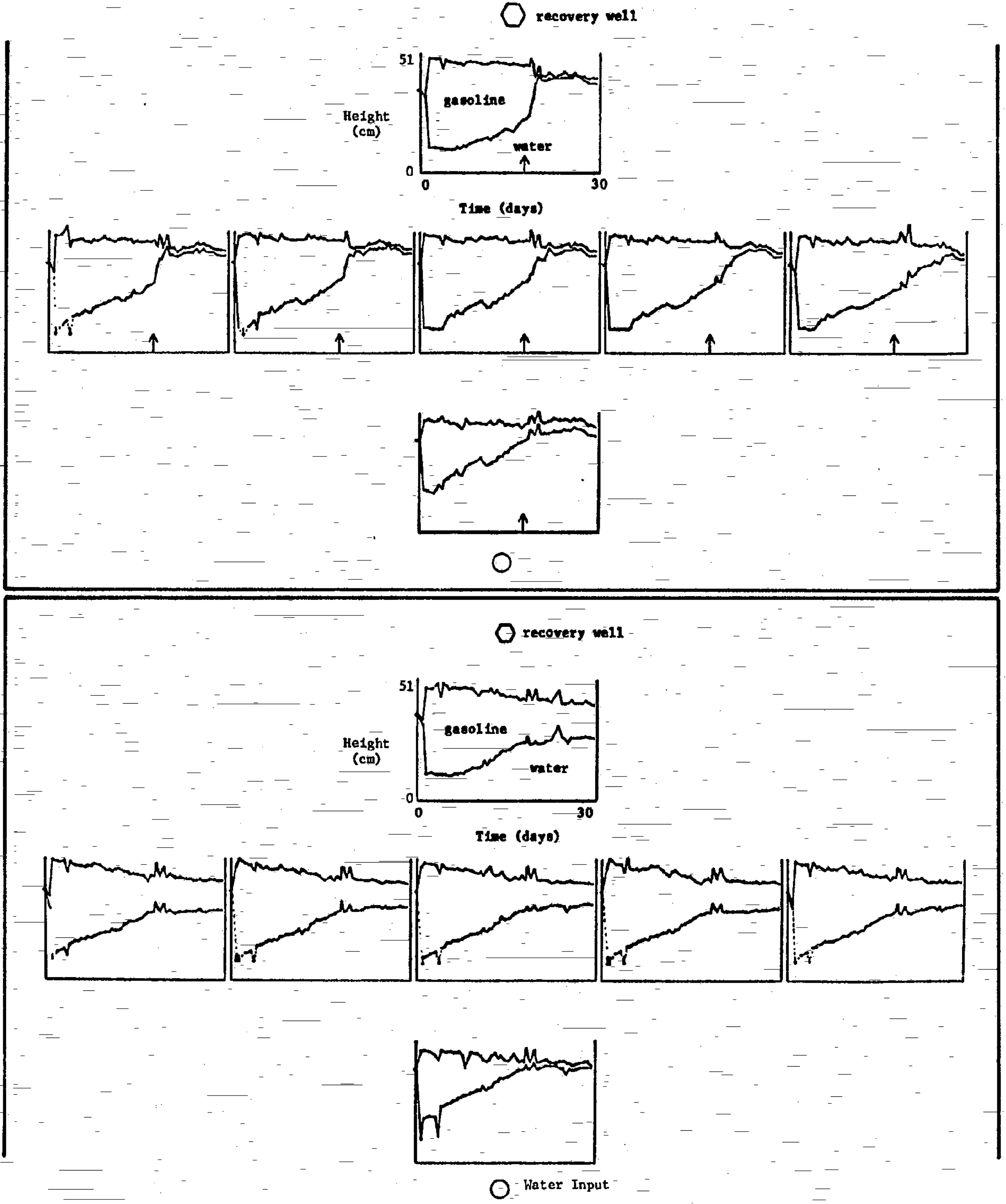

Figure 5

Observation Well Profiles, Phase I Tests

Upper: Surfactant test
Lower: Control test (no surfactant)
↑: Day of surfactant application

back in. It is thought that the dramatic elevation of the water column that occurs following the application of the surfactant is the result of collapse or compression of the capillary fringe caused by the surfactant. This allows a rapid outflux of gasoline from the wells into the soil area which previously contained the capillary zone; the outflowing gasoline is replaced with inflowing water.

Measurements of gasoline removal were terminated on Day 30 of the Phase I tests. On Day 32, four 5.7 cm (2.25 in.) diameter core samples 91.4 cm (3 ft) long were removed from each tank to evaluate its residual gasoline content (only sand above the piezometric level was collected). The core sample sites were evenly spaced along a line from the water input to the standpipe. The gasoline was extracted from the core contents using a CS_2 extraction technique (see Sec. 3.0). The calculated volumes of residual gasoline were 45.3 liters in the control test tank and 55.5 liters in the surfactant test tank.

The volume of gasoline spilled in each test (75.7 liters) is accounted for as follows; values are in liters.

	Test	
	Control	Surfactant
Raw gasoline removed	23.4	15.2
Dissolved gasoline in effluent	6.8	7.8
Residual volume	45.3	55.5
Total	75.5	78.5

That is, nominally 100% of the gasoline spilled in each test was accounted for.

The gasoline that was spilled in each test contained 41% by weight of aromatic heavy fractions. (The heavy fraction is defined arbitrarily as components with six or more carbons.) The gasoline removed from the separators of both test tanks, control and surfactant, averaged 50% heavy fractions throughout the 30 day test period. The gasoline extracted from the effluents of both tests averaged 70% throughout, indicative probably of the greater solubility in water of the aromatic heavy fractions than of the light fractions. Table I summarizes the mass balance for Phase I. Note that while the amounts of gasoline remaining in the tank estimated by difference and from core sample extraction appear to agree, the estimates for light and heavy fractions differ by a factor of two. The heavy fractions are overestimated and the light fractions are underestimated by the core sample analysis. Core sampling would be expected to provide a better estimate of the heavy than of the light fractions because the lower vapor pressure of the former would preclude their loss due to evaporation during both the experiment and the core sampling. If it is assumed that a larger number of core samples would have yielded better estimates for the heavy fractions (i.e., equal to the presumed values of 14.5 liters for the control and 17.9 liters for the surfactant test) and that the relative concentrations of the light and heavy fractions are correct, then the volume of light fraction hydrocarbons not accounted for would have been

$31.0 - \frac{14.5}{30.4} \times 14.9 = 23.9$ liters for the control, and

$34.8 - \frac{17.9}{37.2} \times 18.3 = 26.0$ liters for the sufactant test.

The temperature of each tank was maintained at 13 ± 2°C.

The pH of the source (City of Austin) water varied between 9.7 and 10.0. The pHs of the effluents from the two tanks varied between 9.1 and 9.3. There was a transient (two days duration) depression (0.2 pH)

TABLE I

MASS BALANCE - PHASE I

CONTROL	LITERS (% OF TOTAL)		
	Heavy	Light	Total
gasoline spilled	31.0 (41%)	44.7 (59%)	75.7
raw gasoline removed from separators	11.7 (50%)	11.7 (50%)	23.4
gasoline dissolved in effluent	4.8 (70%)	2.0 (30%)	6.8
gasoline presumed in tank by difference	14.5 (32%)	31.0 (68%)	45.5
gasoline estimated from core sample extracts	30.4 (67%)	14.9 (33%)	45.3

SURFACTANT - SINGLE APPLICATION	LITERS (% OF TOTAL)		
	Heavy	Light	Total
gasoline spilled	31.0 (41%)	44.7 (59%)	75.7
raw gasoline removed from separators	7.6 (50%)	7.6 (50%)	15.2
gasoline dissolved in effluent	5.5 (70%)	2.3 (30%)	7.8
gasoline presumed in tank by difference	17.9 (34%)	34.8 (66%)	52.7
gasoline estimated from core sample extracts	37.2 (67%)	18.3 (33%)	55.5

in the pH of the effluent from the surfactant test tank after surfactant was applied.

As noted in Sec. 3.0, soil and effluent CO_2 and O_2 levels were monitored to assess biodegradation activity. The CO_2 levels in the soil fluctuated widely, ±500 ppm about an approximate mean of 1000 ppm. Although there was a positive correlation in the variation of CO_2 levels in the two tanks, no meaningful interpretation of these data can be provided. The levels of dissolved O_2 in the input and effluent waters remained steady at 2-5 ppm throughout the test duration. The CO_2 levels in the effluents from both tanks exhibited an increasing divergence from the level in the input water during the latter half of the test period, suggesting increased bacterial activity. It is not understood why the increasing CO_2 levels were not accompanied by decreasing O_2 levels. Some of the increase in CO_2 may have been caused by a reaction between acidic by-products (from bacteria) and soil carbonate, and may not be a manifestation of bio-oxidation of the gasoline or the surfactant.

4.2 Phase II

Figure 6 displays gasoline removal during the two tests constituting Phase II of the experimental program: multiple (daily) applications of surfactant by percolation through the soil, and multiple (daily) applications by direct injection into the water table. The format of Fig. 6 is analogous to that of Fig. 3. Shown are plots of volumes of raw gasoline collected from the separators, of surfactant levels in the effluents, of dissolved gasoline levels in the effluents, and of total volumes of gasoline removed. The plots are identified in the figure; the percolation test data are identified by the solid curve. The time span during

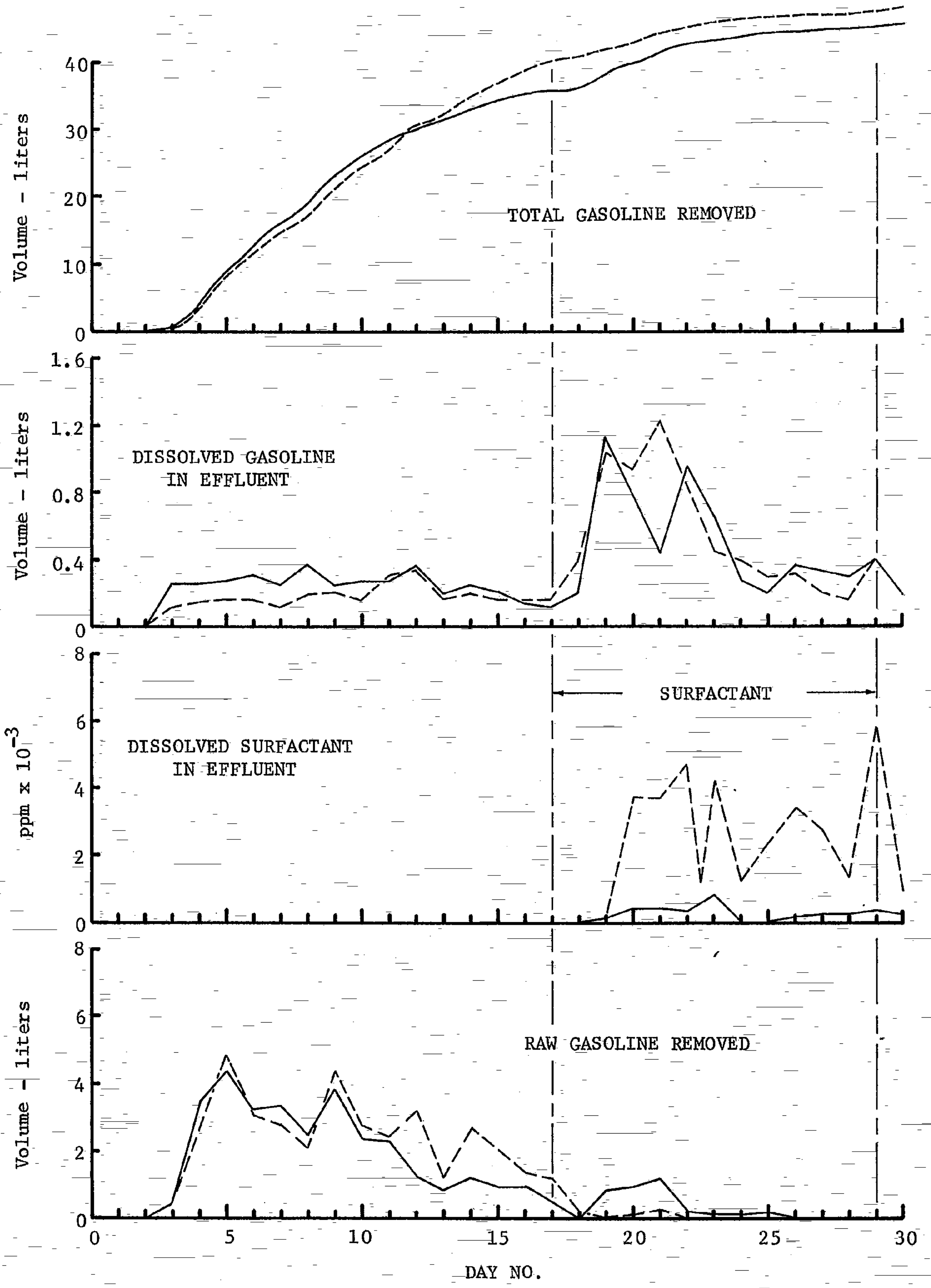

Figure 6

Time Course of Gasoline Removal during Phase II Tests

——Daily percolation of surfactant
– – –Daily injection of surfactant

which surfactant was applied in the two tests is marked by the vertical lines on Days 17 and 29.

The lowest plot shows daily totals of raw gasoline collected from the separators; the ordinate is in liters. The total volume of raw gasoline recovered in the percolation test was 35.6 liters, or 47.0% of the spilled volume; it was 37.6 liters, or 49.7%, in the injection test. The volumes collected prior to the application of surfactant were 32.1 liters and 36.9 liters, respectively, vis-a-vis nominal 15 liters in the tests of Phase I, illustrating the difference in the flow rates of the two sand packs. The volumes of raw gasoline recovered during the surfactant application period totaled 3.5 liters in the percolation test and 0.7 liters in the injection test. This gasoline was collected as an emulsion that was broken by salting out to evaluate the gasoline content.

The second plot up in Fig. 6 illustrates the effluent surfactant concentrations produced by the two application techniques. The ordinate for this plot is ppm (x 10^{-3}). The injection technique obviously yielded higher (about 4X) levels of dissolved surfactant in the effluent than did the percolation method, due in part to adsorption of surfactant by sand in the latter. However, as will become apparent, the impact of this difference on volumes of gasoline removed from the two tanks was negligible. The wide fluctuations in surfactant levels exhibited in this plot are probably due in part to variations in water flow and in part to variations in time of sampling after the daily surfactant spill.

The daily volumes of dissolved gasoline in the effluents are displayed in the third plot up; the ordinate is in liters. There is an approximate five-fold increase in gasoline removed during the first 5-6 days of surfactant application in both tests, after which the daily volumes return to about pre-application levels. The injection technique evidenced slightly more dissolved gasoline removed during the surfactant application period--6.7 liters versus 6.2 liters, or 8.8% and 8.2%, respectively, of the total spilled. These are not statistically different. The total volumes removed were 9.9 and 9.3 liters (13.1% and 12.3%), respectively, in the percolation and injection tests.

The uppermost plot in Fig. 6 shows cumulative curves of total gasoline removed during the Phase II tests. The ordinate is in liters. The total volume recovered during the daily surfactant percolation test was 45.5 liters, or 60.1% of the volume spilled; the volume recovered during the surfactant injection test was 46.9 liters, or 62.0%. The difference is not significant.

Figure 7 is a plot of daily volumes of gasoline recovered from the separators plus that dissolved in the effluents. This figure highlights the enhanced recovery effected by the application of surfactant (via either technique). Again, the Phase II curves are not statistically different.

Figure 8 displays the daily gasoline and water levels measured in the seven observation wells of each tank (see Figs. 1 and 2). The measurements for the percolation test tank are shown by the lower set of profiles; those for the injection tank, by the upper set. The indicated location of the standpipe/recovery well indexes these data to the plan view shown in Fig. 1. The arrow in each plot indicates the first day of the surfactant application period (through Day 29). It is obvious from these data that the gasoline was distributed less uniformly across the water table during these tests than it was during the Phase I tests, and there was notably less lateral distribution in the percolation test tank than in

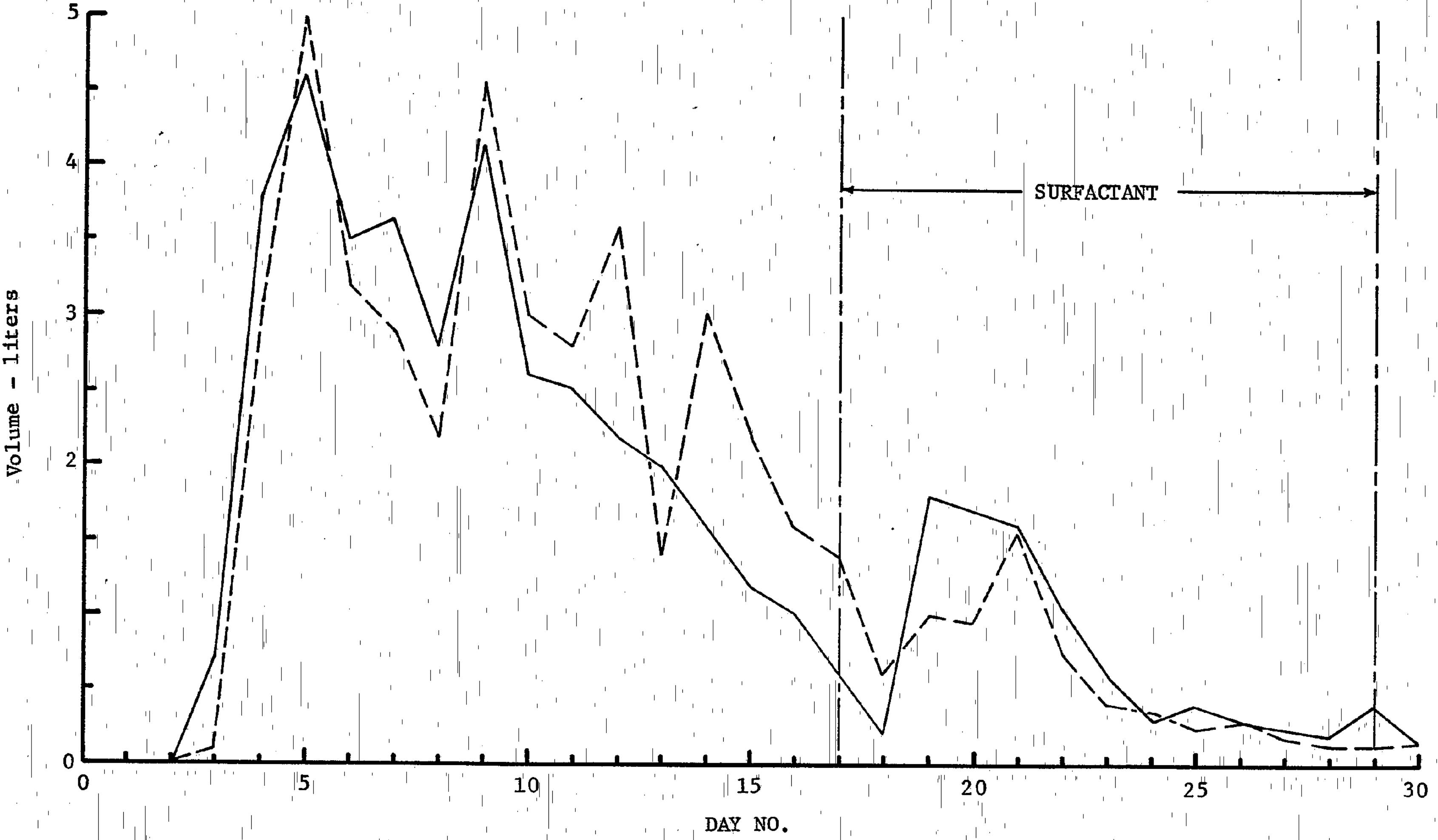

Figure 7

Daily Volumes of Gasoline Removed from Separators and Effluents
Phase II

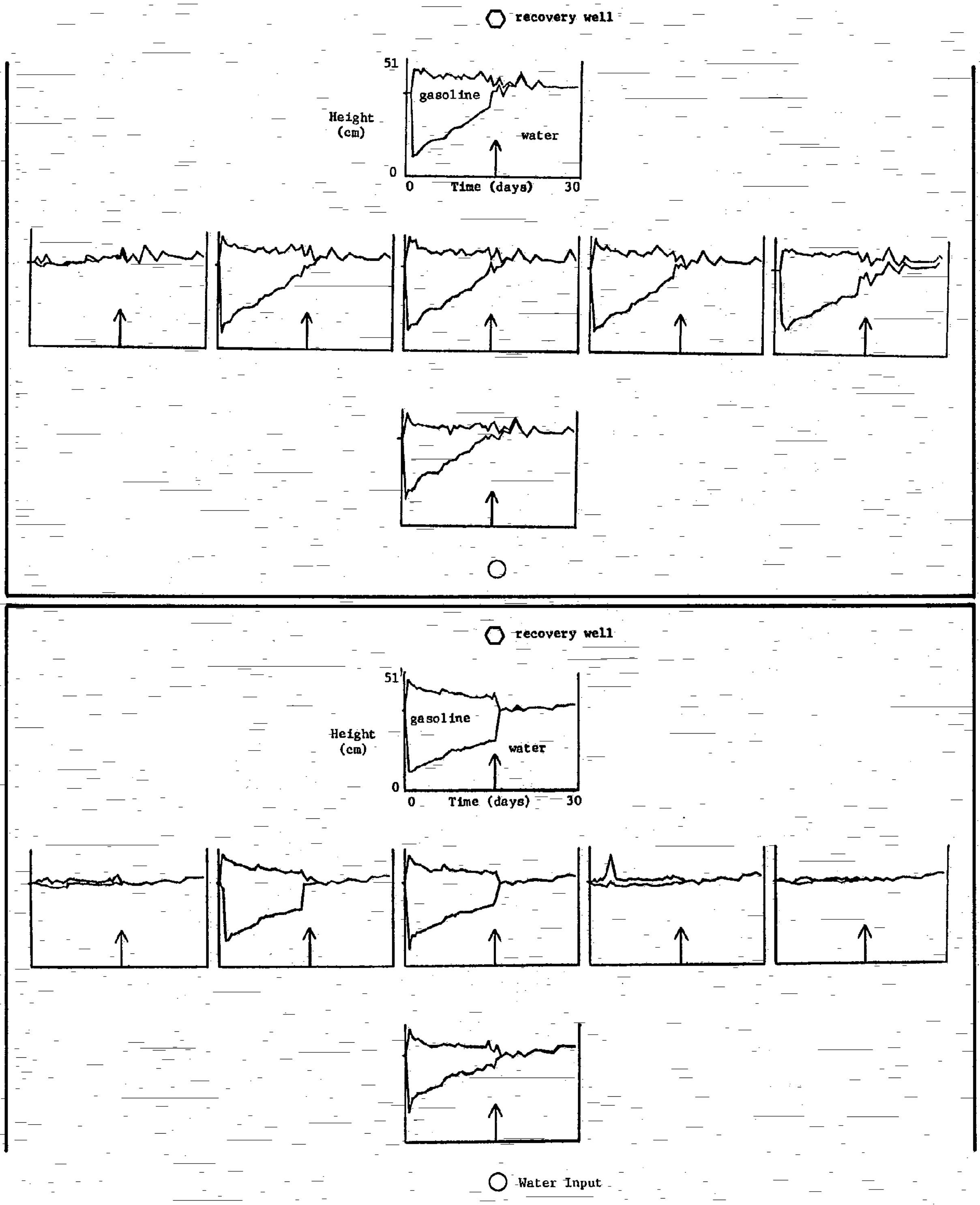

Figure 8
Observation Well Profiles, Phase II Tests

Upper: Daily injection test
Lower: Daily percolation test
↑: 1st day of surfactant application

the injection test tank. Factors that may have contributed to these variations are 1) different overall sand permeabilities between Phases I and II, as well as local permeability inhomogeneities within each tank and 2) a different gasoline spill rate in Phase I than in Phase II.

Measurements of gasoline removal were terminated on Day 30. On Day 31, core samples were removed from each tank to evaluate residual gasoline content. Since the gasoline distribution (see Fig. 8) was obviously less uniform than during the Phase I tests, nine instead of four core samples were removed from each tank (the tank was divided into a 3 X 3 grid, with a sample removed from the center of each grid square). The gasoline was extracted from the core contents using the CS_2 extraction technique. Four of the nine core samples taken from the percolation test contained no gasoline at all, reinforcing the observation well data that indicated a poorly distributed gasoline layer. The calculated volumes of residual gasoline were 9.5 liters, or 12.5% of the volume spilled, in the percolation tank, and 6.0 liters, or 7.9%, in the injection tank.

Accountability of the volume (75.7 liters) of gasoline spilled in each tank was as follows; values are in liters.

	Test	
	Daily Percolation	Daily Injection
Raw gasoline removed	35.6	37.6
Dissolved gasoline in effluent	9.9	9.3
Residual volume	9.5	6.0
Total	55.0	52.9

That is, about 72% of the gasoline spilled in the two tanks was accounted for.

There is no a priori reason for suspecting errors in the core sample measurements. The approximately 25 liters unaccounted for in each test are assumed to have been lost in the effluent, i.e., were missed because of the low effluent sampling rate (only twice daily; peak levels of dissolute could have occurred during nonsampled periods). It was speculated that the high surfactant levels in the effluent might have interferred with the CS_2 extraction of the gasoline, but tests revealed that the effect was negligible (less than 6% decrement).

The gasoline spilled in each tank during these tests contained 33% by weight of aromatic heavy fractions. The raw gasoline recovered from the separators averaged 40% heavy fractions throughout the test period. The gasoline extracted from the effluents of both tests averaged 70% heavy fractions during the first two weeks of the experiment. During the first four days of surfactant applications the content of heavy fractions decreased to an average of 50% and remained fairly constant through the end of the test period. This decrement illustrates the effectiveness of the surfactant in increasing the solubility of the lighter fractions.

Tank temperature was maintained within the same limits observed during the Phase I tests. The pHs of the effluents from the two tanks varied between 8.8 and 9.4.

The levels of CO_2 in the sand packs of both tanks increased in parallel during the 30 day test period from nominal 1000 ppm on Day 1 to nominal 16,000 ppm on Day 29, indicating an increase in bacterial activity. Levels of O_2 in the input and effluent waters remained unchanged at 5 ppm throughout the test period. CO_2 levels in the input and effluent waters were essentially identical and remained unchanged at 30 ppm until the beginning of the surfactant application period. At that time, the levels in the effluents began increasing, indicating probable bacterial metabolism of the surfactant; the highest levels occurred in the surfactant injection test.

4.3 Properties of Hydrophone Solutions

It is apparent from the preceding results and discussion that a significant portion of gasoline spilled, approximately one-third, could not be readily accounted for. Examination of the relative amounts of light and heavy hydrocarbons in the gasoline recovered leads to the conclusion that the unaccounted-for product must be in the light fractions. Losses due to evaporation are strongly suspected.

Table II presents some properties of three hypothetical solutions of aliphatic hydrocarbons. It is not suggested that these blends are representative of the gasolines used in the present experiments. But they illustrate the effects of changing the ratio of light to heavy fractions in hydrocarbon solutions. Solutions 1, 2 and 3 contain roughly 30%, 60% and 85% by weight of light (C_4 to C_6) fractions as defined in Sec. 3.0. The equilibrium vapor pressures over the solutions, calculated on the basis of Raoult's law, are seen to increase in proportion to the amount of light hydrocarbon present inthe liquid phase. A considerable mass of hydrocarbon can exist in the vapor phase over the liquid as shown by the columns labeled Condensed Equivalent Volume. The mass of hydrocarbons in the vapor phase also increases in proportion to the amount of light fractions in the liquid.

The hydrocarbon vapors formed during the experiments were not analyzed. However, the raw gasoline, as well as the gasoline recovered by extraction from the effluent water, was richer in heavy fractions than the gasoline spilled, which indicates that the residual gasoline in the tank was richer in light fractions. Since the pore volume over the

Table 2

Properties of Three Solutions of Aliphatic Hydrocarbons

Component	MW	Density g/cc	Vapor Pressure atm at 20°C	Mole Fraction in Liquid			Weight % in Liquid			Partial Pressure of Vapor			Condensed Equivalent Vol. in l of 1 m³ of Vapor		
				Soln 1	Soln 2	Soln 3	Soln 1	Soln 2	Soln 3	Soln 1	Soln 2	Soln 3	Soln 1	Soln 2	Soln 3
n $C_4 H_{10}$	58	.60	2.5	0.05	0.15	0.25	2.9	10.1	18.9	0.125	0.375	0.625	0.54	1.61	2.70
n $C_3 H_{12}$	72	.62	0.7	0.15	0.30	0.35	10.4	25.1	32.9	0.105	0.210	0.245	0.54	1.08	1.27
n $C_6 H_{14}$	86	.66	0.2	0.20	0.25	0.30	17.2	25.0	33.7	0.040	0.050	0.060	0.23	0.29	0.35
n $C_7 H_{16}$	100	.68	0.06	0.20	0.15	0.05	20.0	17.5	6.5	0.012	0.009	0.003	0.08	0.06	0.02
n $C_8 H_{18}$	114	.70	0.02	0.20	0.05	0.03	22.8	6.6	4.5	0.004	0.001	0.001	0.03	0.01	0.01
n $C_9 H_{20}$	128	.72	0.006	0.15	0.05	0.01	19.2	7.5	1.7	0.001	0.000	0.000	0.01	0.00	0.00
n $C_{10}H_{22}$	142	.75	0.002	0.05	0.05	0.01	7.1	8.2	1.8	0.000	0.000	0.000	0.00	0.00	0.00
										0.287	0.645	0.934	1.43	3.06	4.35

gasoline spill was about 2.3 m^3, the preceding example (Table II) suggests that the equivalent condensed volume of hydrocarbon vapor could have been as high as 10 liters at the end of the experiments. The core sampling procedure used had no provision to capture vapor phase hydrocarbons. Thus, up to one-half of the unaccounted-for light hydrocarbons could have been lost in the process of taking the core samples.

Precautions taken to minimize evaporative losses from the tank included a concrete cap and a sprayed-on urethane foam seal. Penetrations through the cap for vapor wells and observation wells were sealed with a silicone caulking compound. Subsequent work on forced air venting* performed in the same facility showed that these precautions were insufficient to provide a pressure-tight enclosure. This leads us to conclude that as the hydrocarbon vapor pressure increased with time the tank permitted hydrocarbon vapor and air to escape thereby maintaining a one atmosphere (nominal) pressure inside.

4.4 Surfactant Effectiveness

In retrospect, it is unfortunate that a control experiment was not included in Phase II. Had the sand packs for the two phases been similar in permeability it would have been possible to make direct day-by-day comparisons between the gasoline eluted from the control tank and that eluted from the tanks in Phase II. The contol experiment of Phase I may, however, be compared if the time associated with gasoline elution is resealed using the ratio of the permeabilities of the sand packs in the two phases as a multiplicitave factor. Fig. 9 presents the result of this exercise. While not conclusive, Fig. 9 strongly suggests that the

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* Texas Research Institute, Inc., "Forced Venting To Remove Gasoline Vapor From A Large-Scale Model Aquifer," TRI Rpt. No. 82101-F:TAV (12 July 1983).

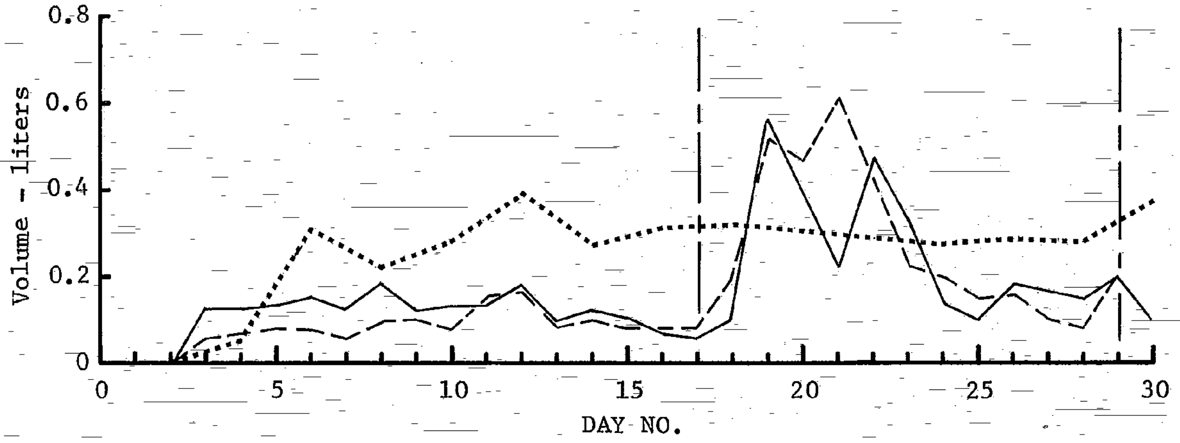

Figure 9

Dissolved Gasoline in Effluent during Phase II Tests

•••••• Rescaled control test (no surfactant) from Phase I

——— Daily percolation of surfactant

– – – Daily injection of surfactant

increased volume of gasoline recovered during the application period of the Phase II tests was a result of the surfacant treatments. Using the rescaled control test as a guide, the Phase II tests had just about completed the initial large yield of gasoline by gravity drainage and were beginning the slow dissolved-hydrocarbon-only yield at the time surfactant treatment began. The surfacant induced "kick" in gasoline recovery has been observed previously* in column studies shown in Fig. 10.

Based on the estimate by difference of residual heavy fractions of gasoline in the control test and the ratio of heavy fractions to light fractions determined by core sampling, it is estimated that the actual residual liquid product in the tank at the completion of the 30 day control test was 14.5 liters heavy fraction, 7.2 liters light fraction, 21.7 liters total, with most of the residual light fractions being lost to evaporation. Had the control test been continued for another 30 days, an additonal 3-4 liters of gasoline would probably have eluted in dissolved form or been lost to evaporation, leaving about 18 liters of residual gasoline. It is assumed that a 60 day control test would be equivalent to the 30 day Phase II tests because of the difference in sand pack permeabilities.

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*Texas Research Institute, Inc., "Underground Movement of Gasoline on Groundwater and Enhanced Recovery by Surfactants," Final Report (September 14, 1979) submitted to the American Petroleum Institute.

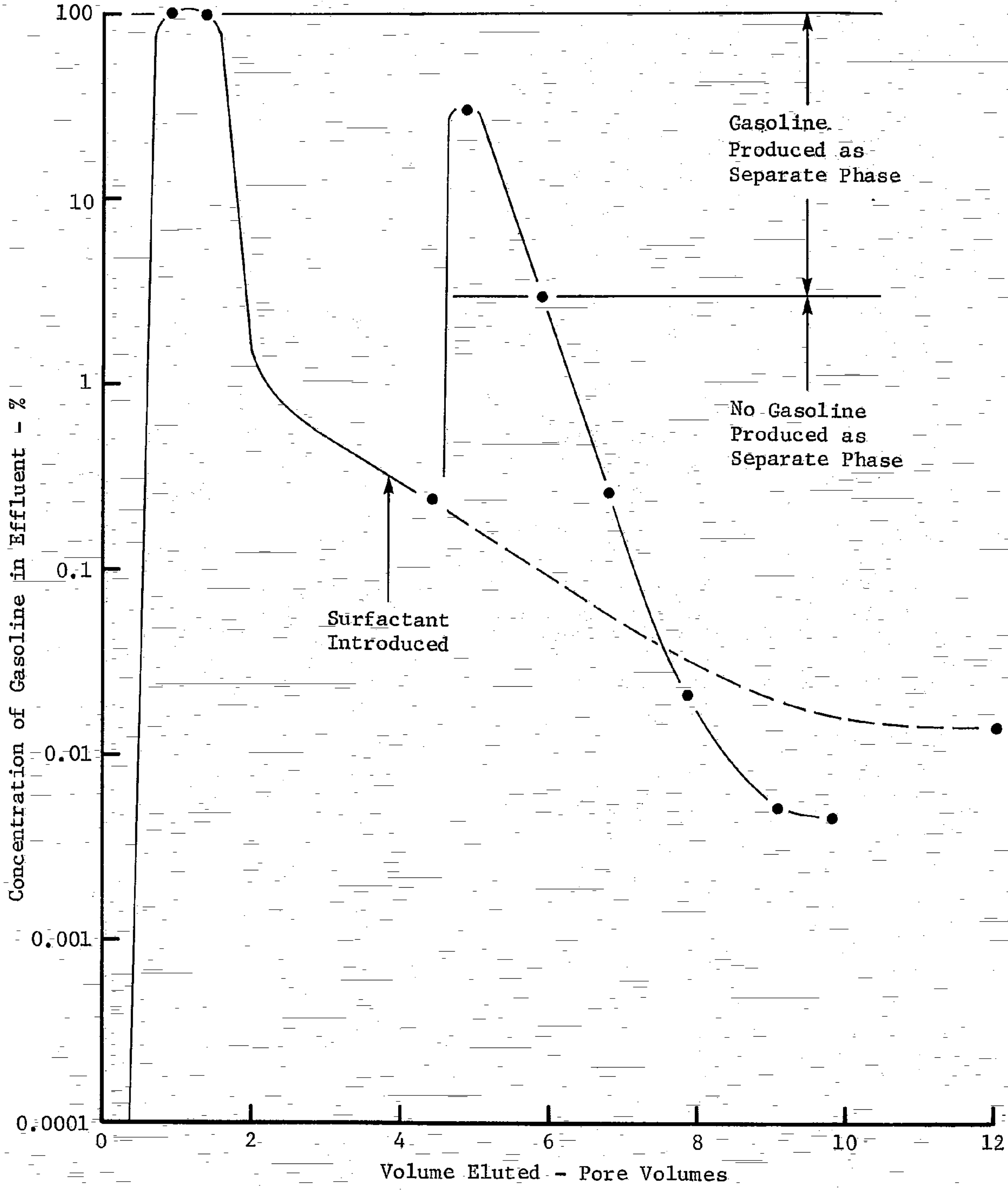


Figure 10

Displacement of Gasoline from a Sand Pack by Water and by a 2% Richonate-YLA, 2% Hyonic PE-90 Aqueous Surfactant Solution

Similarly, it is estimated that the residual liquid volumes in the tanks at the completion of Phase II tests were:

Percolation Test

5.0 liters heavy fraction
4.0 liters light fraction

9.0 liters total

Injection Test

4.7 liters heavy fraction
2.0 liters light fraction

6.7 liters total

again, with most of the residual light fractions being lost to evaporation. By this method of analysis, the surfactant treatments reduced the residual gasoline concentration by a factor of two or three, with the injection technique appearing to be the better. On the other hand, based on Table II and the suggestion that the gasoline recovered after Day 18 was due to surfactant treatment, the percolation technique was more effective than the injection technique (9.3 liters vs. 7.0 liters recovered during Days 18-30).

5.0 CONCLUSIONS AND RECOMMENDATIONS

Two factors cloud the results of this work. The first was a difference in permeability between the sand packs in the two phases. The problems caused by this difference could have been avoided by running a second control experiment in Phase II, but this was not done because of cost. The second factor was the inability to achieve closure with mass balances. This problem is fundimental in nature. It appears to be related to the high vapor pressure that exists over aging hydrocarbon solutions. As discussed later, it can be corrected by changing the facility design and gasoline sampling procedures. However, evaporative loss of hydrocarbons, even at the level (30%) presumed in the present work, does not totally obscure how much gasoline was removed after surfactant treatment or how much was left in the tank at the end of the test.

The results of the Phase I work show that a single application of a 2% Richonate YLA plus 2% Hyonic PE-90 aqueous solution is not effective in mobilizing spilled gasoline. The level of surfactant in solution achieved by this technique was on the order of several parts per million as measured in the effluent water. The results of the Phase II tests show that more aggressive surfactant treatments are effective in mobilizing raw gasoline and in increasing its solubity in water. The level of surfactant concentration in the effluent water achieved during Phase II was two to three orders of magnitude greater than that reached during Phase I. And this was achieved only after double to triple amounts of surfactant were added (i.e., after two to three days of application). Most of the effect of surfactant treatment was observed to occur during the first four to six days of treatment, suggesting that about twice as much surfactant was applied as was actually needed. Quantification of these results is not conclusive because of the lack of a satisfactory control; however, it is estimated that the surfactant treatments reduced the residual gasoline levels in the tank by a factor of two to three. Another way of expressing the effectiveness of surfactant treatment is to gage the time saved over the traditional gravimetric recovery method. Seven to nine liters of gasoline were recovered within a short period of time after surfactant treatment. A normal recovery rate of 0.1 liter per day without surfactant treatment would have required 70-90 days to achieve similar results.

It is concluded that application of surfactant to residual gasoline in an aquifer effectively decreases the amount of residual gasoline.

The results of the present work constitute a step forward in spilled gasoline recovery technology. However, it is clear that additional work is necessary before full-scale field tests can be undertaken with a degree of confidence commensurate with the cost.

To achieve closure in mass accountability would require either a pressure tight experiment chamber in which the hydrocarbon composition is continuously monitored, or a secondary enclosure around the experiment tank for monitoring evaporative loss of hydrocarbon vapors. The latter would be accomplished by purging the secondary chamber with a known volume rate of air and monitoring the effluent for hydrocarbon vapor.

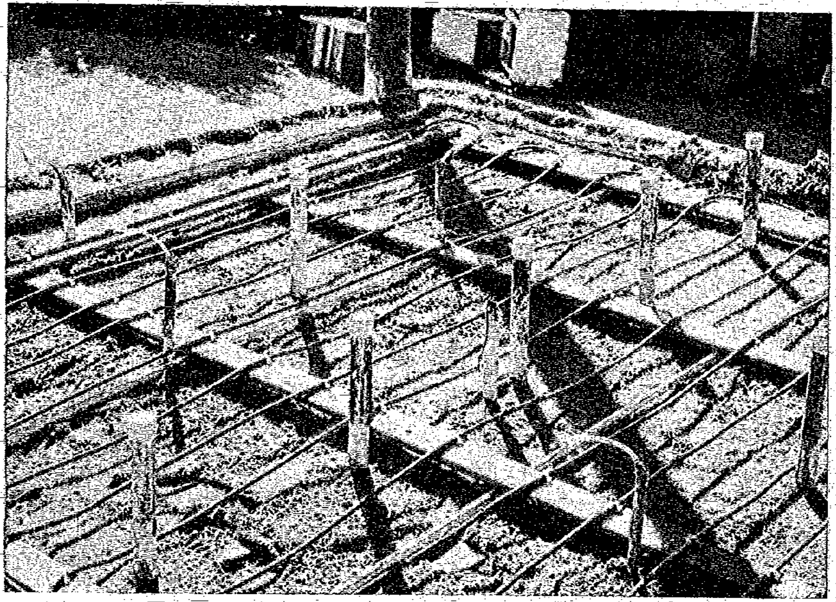
Only one surfactant solution was assessed in the present work. It was a best choice based on earlier laboratory studies performed at TRI. The effectiveness of other surfactants, or of different solutions (or sequential applications) of the same surfactants, in sand, and in other soils, should be evaluated. Such evaluation should include other promising surfactant solutions and use several different types of soil. Initial work should be performed on a laboratory scale, with a modified model aquifer facility as discussed. Such work would provide verification of the present results and guidelines for implementing and evaluating a full-scale test.

The present work employed two techniques for applying the surfactant solution: percolation and injection. While both techniques appeared to be effective, neither has been optimized. A combination of these two techniques, either in a sequential or a parallel format, might further enhance recovery of the entrapped gasoline. Other feasible surfactant application techniques could be assessed in a model aquifer facility using different types of soil. Again, this work would provide meaningful guidelines for full-scale applications.

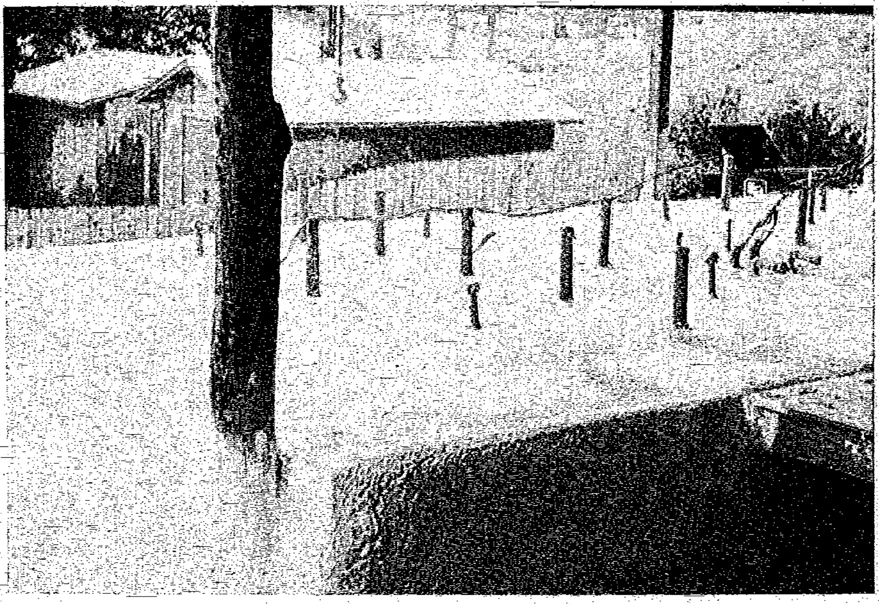
Finally, the results of the present work underscore the uncertainties in predicting distribution and flow behaviors in even simply structured soils. An effective surfactant solution and/or application technique could be disregarded through failure to appreciate the fluid flow dynamics for a particular soil and the parameters that influence them. For example, how is the distribution of the surfactant affected by spill rate? Does injected surfactant diffuse smoothly and evenly through the contaminated medium, or does it, under some conditions, undercut the capillary fringe and thereby miss treating the contaminated region? What is the optimum surfactant injection rate as a function of natural flow through the aquifer? In future studies, increased effort--including requisite instrumentation--should be applied to understanding this facet of the problem. This will permit more realistic assessment of the model study results and their extrapolation to full-scale testing.

Appendix A

Photographs of TRI Soil/Aquifer Model Facility



Photograph of surface of sand-filled tank showing observation well and vapor well extensions and thermocouple pipes, top of rainmaker, and copper tubing for cooling water.



Photograph of surface of tank after spraying with polyurethane foam showing observation well, vapor well, and thermocouple pipe extension.

Appendix B

Calculation of Soil Gasoline Saturation Values

The following assumptions were made for estimating available soil pore space:

1. The residual gasoline occupies a 15.25 cm (6 in.) thick sand layer.
2. The residual gasoline is uniformly distributed throughout the sand layer.
3. Water saturation varies linearly from 100% at the lower boundary to 20% at the upper boundary of the sand layer. Therefore, only 40% of the available pore space is free of water and can hold gasoline.

The available volume (V_A) is calculated from

$$0.4 \phi V_S$$

where ϕ is the porosity (0.34) and V_S is the volume of the sand layer. That is,

$$V_A = 0.4 \times 0.34 \times 3.05 \text{ m} \times 3.05 \text{ m} \times 0.1525 \text{ m}$$
$$= 0.193 \text{ m}^3$$
$$= 193 \text{ liters}$$

The residual gasoline volumes (V_R) prior to surfactant application were:

53.0 liters, control test,
59.0 liters, single application test
39.8 liters, multiple percolation test, and
36.2 liters, multiple injection test,

giving percent saturation ($V_R/V_A \times 100$) values of:

27.5,
30.6,
20.6, and
18.8, respectively.

The residual gasoline volumes (V_r) after surfactant application were:

45.3 liters, control test,

55.5 liters, single application test,

9.5 liters, multiple percolation test, and

6.0 liters, multiple injection test,

giving percent saturation (V_r/V_A X 100) values of:

23.5,

28.8,

4.9, and

3.1, respectively.

Appendix C

Surfactant Analysis and Sand Characterization

Surfactant Analysis

The surfactant solution used in these studies was a mixture of two surfactants - Richonate YLA (anionic) and Hyonic PE-90 (nonionic). To establish the most effective way of monitoring surfactant concentration in the effluent, standardized analytical procedures were applied to solutions of each surfactant alone and to the mixture so that analytical interferences, if any, could be identified.

I. RICHONATE YLA ANALYSIS

A. The LaMotte Chemical Detergent Test Kit

The LaMotte test kit analyzes 5 ml samples of alkyl benzene sulfonate (YLA) in the range of 1-6 ppm with an accuracy of ± 0.5 ppm. The presence of PE-90 does not interfere with this test. The test kit can be used for preliminary analysis of surfactant samples and will help determine the dilutions to be used in the more sensitive methylene blue analysis.

B. Methylene Blue Analysis

The ASTM (D 2330) method is used for the analysis of Richonate YLA, an alkylaryl sulfonate. This method employs colorimetric determination of a methylene blue-YLA complex. When the reagents are used in the proportions described below, the method is accurate for YLA solutions of 0-5 ppm.

1. Reagents

- Chloroform ($CHCl_3$).
- Methylene Blue Solution - Dissolve 0.1 g of methylene blue chloride in 100 ml of water. Transfer 30 ml of this solution to a 1 liter volumetric flask and add 500 ml of water. Add 7 ml of concentrated H_2SO_4 (sp gr 1.84) and 50 g of $NaH_2PO_4{:}H_2O$. Shake until solution is complete and then dilute to 1 liter with water.

- <u>Phenolphthalein Indicator Solution (5.0 g/liter)</u> - Dissolve 0.5 g of phenolphthalein in 50 ml of 95% ethyl alcohol and dilute to 100 ml with water.

  Note: Specially denatured ethyl alcohol conforming to Formula No. 3A or 30 of the U.S. Bureau of Internal Revenue may be substituted for 95% ethyl alcohol.
- <u>Sodium Alkyl Benzene Sulfonate, Stock Solution</u> - Weigh the amount of reference material necessary to provide the equivalent of 1.0000 g of ABS on a 100% active basis. Dissolve in water and dilute to 1 liter.
- <u>Sodium Alkyl Benzene Sulfonate, Standard Solution</u> (1.0 ml = 0.01 mg ABS) - Dilute 10.0 ml of the stock ABS solution to 1 liter with water.
- <u>Sodium Hydroxide Solution</u> (10 g/liter) - Dissolve 10 g of sodium hydroxide (NaOH) in water and dilute to 1 liter.
- <u>Sodium Phosphate, Acidified Wash Solution</u> - Dissolve 50 g of sodium dihydrogen phosphate monohydrate ($NaH_2PO_4{:}H_2O$) in 500 ml of water in a 1 liter volumetric flask. Add 7 ml of concentrated sulfuric acid (H_2SO_4, sp gr 1.84) and dilute to volume with water.
- <u>Sulfuric Acid</u> - Carefully add 7 ml of concentrated sulfuric acid to water and dilute to 1 liter with water.

2. Procedure

- A 25 ml sample is placed in a 60 ml separatory funnel.
- One drop of phenolphthalein is added.
- Drops of NaOH are added to turn solution pink.
- Drops of H_2SO_4 are added until solution is just clear again.
- 7 ml of methylene blue are added and the funnel is shaken.

- Approximately 6 ml of chloroform ($CHCl_3$) are added and mixed well by shaking. Once the phases separate, the $CHCl_3$ layer is drained into an Erlenmeyer flask.
- Two more $CHCl_3$ washes are done. The aqueous layer is then discarded and the $CHCl_3$ layer is put back into the separatory funnel.
- 25 ml of phosphate wash solution are added and the funnel is agitated for 30 sec, swirled vertically, and the solutions are allowed to settle for 1 min. The $CHCl_3$ layer is filtered through glass wool into a 25 ml volumetric flask.
- 5 ml of $CHCl_3$ are used to wash the remaining aqueous layer, and are then filtered into the volumetric flask. The flask contents is then brought up to 25 ml with $CHCl_3$, mixed well, and a 1 cm cuvette is filled. The absorbance of the solution is measured at 652 nm on a Beckman DU Spectrophotometer versus a $CHCl_3$ blank.

3. Calibration (see Fig. C1)

Analyses performed on four different days were used to construct a calibration line for the YLA determination. The following data were used:

Date	Concentration ppm	Absorbance*
8-27-81	0	0.010
	1.2	0.062
	2.0	0.110
	3.2	0.152
	4.0	0.192
8-28-81	0	0.007
	1.2	0.063
	2.4	0.120
	4.0	0.196
	6.0	0.282
	7.2	0.323

Date	Concentration ppm	Absorbance*
8-31-81	0	0.011
	3.2	0.148
	6.0	0.267
9-08-81#	0	0.008
	2.0	0.098
	4.0	0.184
	6.0	0.248

*average of at least 2 absorbance readings

#a new standard solution was used here

The system seemed to saturate around 6 ppm, so the calibration line was calculated for all points from 0-5 ppm (excluding the 9-08-81 data).

Slope = 0.0456 absorbance unit per ppm
Intercept = 0.0095
Correlation = 0.9982

On each day of analysis, two reference samples were measured to check this line.

II. HYONIC PE-90 ANALYSIS

The colorimetric determination of non-ionic surfactants discussed by Brown & Hayes* was used with some modifications for the analysis of Hyonic PE-90, a polyethoxylated nonylphenol. When reagents are used in the proportions given below, the method is useful for PE-90 solutions from 400-900 ppm.

A. Reagents

- Chloroform ($CHCl_3$)
- Cobalt Nitrate - 60 g are dissolved in deionized (DI) water in a 1 liter volumetric flask and brought to 1 liter total volume.
- Ammonium Thiocyanate - 400 g are dissolved in DI water in a 1 liter volumetric flask and brought to 1 liter total volume.

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*Analyst 80:755 (1955).

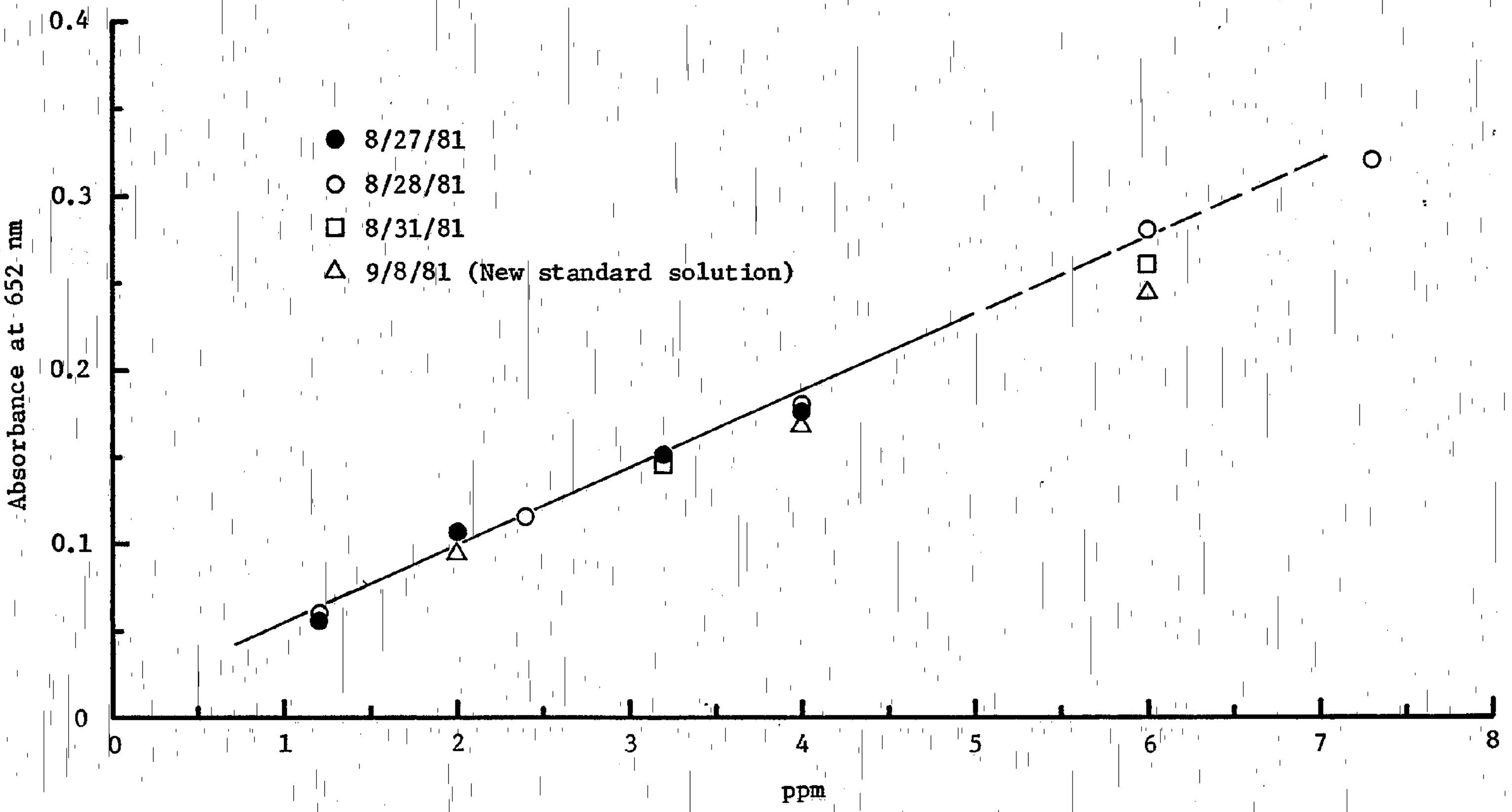


Figure C1
Calibration Line for YLA Analysis

- Cobaltothiocyanate Reagent (CTC Reagent) - Equal volumes of the cobalt nitrate and ammonium thiocyanate solutions are mixed well.

B. Procedure

- A 15.0 ml sample is put into a 60 ml separatory funnel.
- 40 ml of CTC Reagent are added, shaken for 1 min and allowed to react for at least 5 min.
- 6 ml of $CHCl_3$ are used to wash the aqueous solution three times. It is important that this mixture be shaken vigorously for at least 1 min each time. The $CHCl_3$ is drained into a 25 ml volumetric flask. The solution is brought up to 25 ml with $CHCl_3$. If the solution is cloudy, it is centrifuged in a stoppered test tube for about 3 min at a medium speed. This brings the water to the top of the suspension. A 1 cm cuvette is filled with the $CHCl_3$ solution, and the absorbance at 620 nm is measured against a $CHCl_3$ blank. A Beckman DU Spectrophotometer is used for all measurements.

C. Calibration (see Fig. C2)

The reproducibility of this analysis depends on the sample concentration. Above 400 ppm, data are widely scattered, but between 100-300 ppm they are fairly constant. The latter range will be used and the calibration line calculated for data from 100-300 ppm only:

Date	conc. (ppm)	absorbance
9/10/81	133	0.028
	133	0.024
	200	0.036
	200	0.042
	267	0.053
	267	0.051
9/13/81	200	0.041

slope = 0.000194

intercept = 0.000480

correlation = 0.978

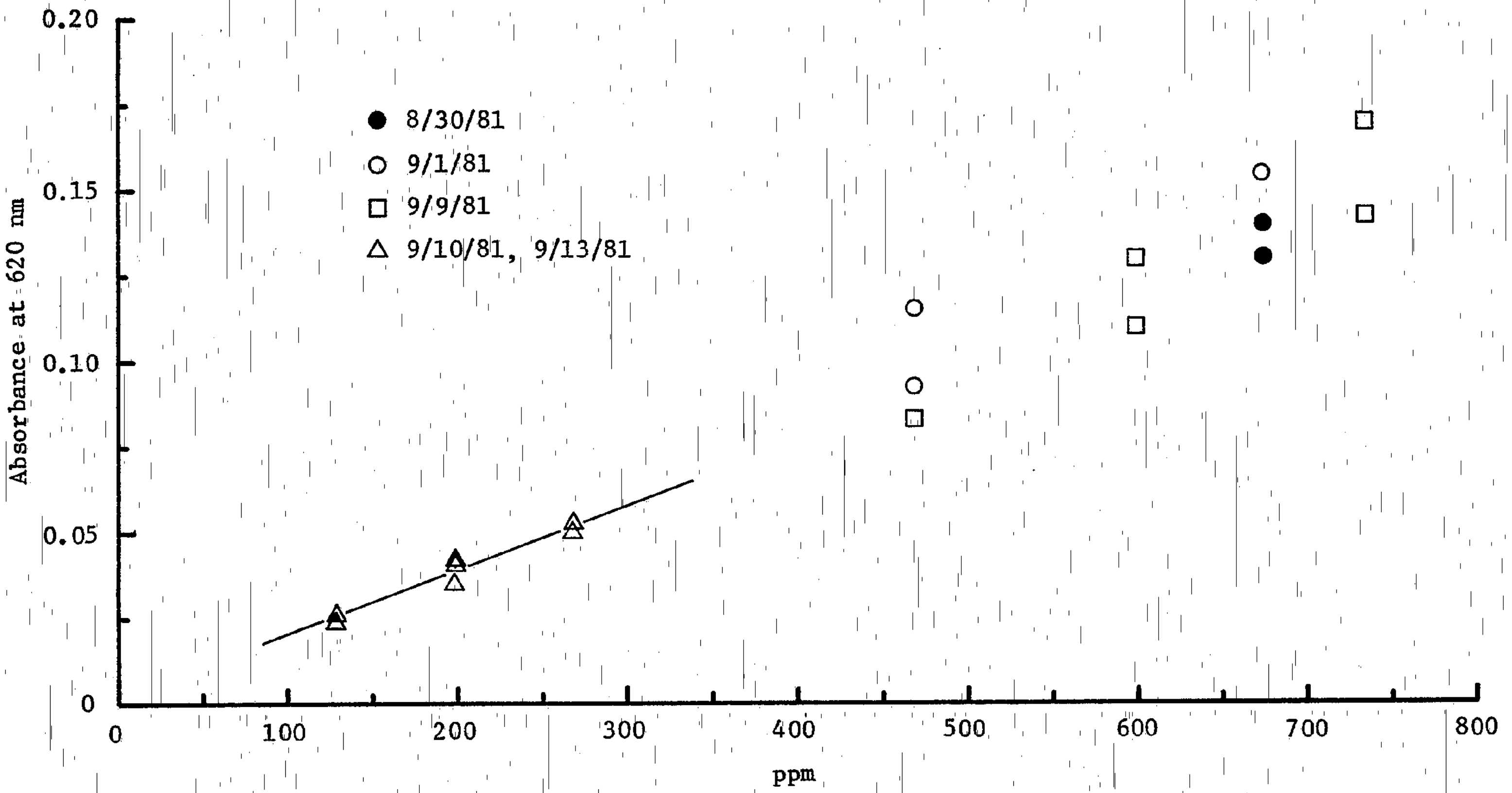


Figure C2
PE-90 Calibration Data

The following data appear on the graph but were not used for calibration:

Date	conc. (ppm)	absorbance
8/30/81	667	0.146
	667	0.138
9/1/81	470	0.114
	470	0.096
	667	0.157
	940	0.237
9/9/81	470	0.085
	600	0.110
	600	0.129
	734	0.169
	734	0.146
	867	0.158

III. ANALYTICAL INTERFERENCE

In several experiments it was shown that the presence of PE-90 does not affect the determination of YLA with methylene blue:

	conc. YLA (ppm)	conc. PE-90 (ppm)	absorbance
8/26/81	10	0	0.465
	10	0	0.459
	10	10	0.469

8/31/81 with the LaMotte Test Kit:

tests done with (a) 2 ppm YLA + no PE-90 and with (b) 2 ppm YLA + 2 ppm PE-90 were identical.

It appeared, though, that YLA interfered with the PE-90 test:

	conc. PE-90 (ppm)	conc. YLA (ppm)	absorbance
8/27/81	667	0	0.200
	667	0	0.182
	667	333	0.062
9/16/81	200	200	0.105
	200	0	0.037
	calibration line value		0.039

conc. PE-90 (ppm)	conc. YLA (ppm)	absorbance
267	267	0.076
267	0	0.056
calibration line value		0.052

For this reason, the YLA analysis was used to monitor the effluent in all tests.

Characterization of Sand

The following properties were evaluated for each batch of sand; porosity, permeability, capillary height, particle size distribution, and surfactant adsorption.

I. POROSITY

The difference in weight between a volume of dry sand and an equal volume of water-saturated sand (packed with a vibrator and degassed) was used to determine the pore volume of the sample. The ratio of pore volume to total volume yields the porosity,

$$\frac{\text{pore volume}}{\text{total volume}} = \text{porosity}$$

At least two determinations were run for each sand batch.

II. PERMEABILITY

A 6.4 cm diam (2.5 in.) sand column was packed with a vibrator and set up as shown in Fig. C-3. The water level in the upper reservoir maintained a constant pressure head above the sand. Water was allowed to flow through the column for 5 min, after which the volume of water eluted from the lower reservoir was measured for 10 min. At least four 10 min periods were monitored for each column and at least three columns were prepared for each sand batch.

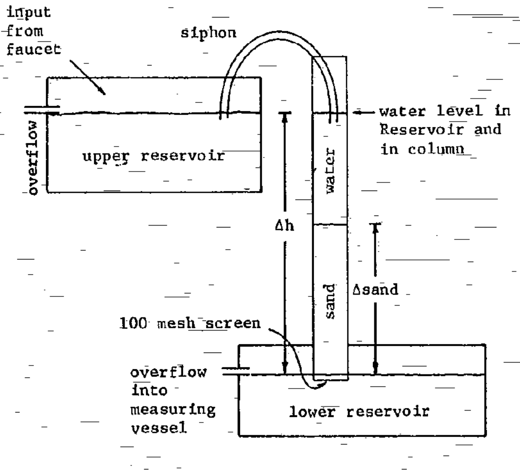


Figure C-3
Permeability Apparatus

The average flow rate for each column was used to evaluate the permeability, in darcies, using the following equation:

$$\text{Permeability (darcies)} = \frac{\eta\left(\frac{Q}{A}\right)}{\frac{dp}{dl}}$$

where n = viscosity of water in centipoise (cP),

Q = flow rate through column (cm^3/sec),

A = cross sectional area of column (cm^2),

dp = pressure head of water (atm), and

dl = length of sand column.

III. CAPILLARY HEIGHT

A 6.4 cm (2.5 in.) diam drained, packed sand column was used to estimate capillary height. Flexible, transparent tubing was fastened to the bottom of the glass column; water was added through the tube to provide a piezometric water level 15 cm (6 in.) above the bottom of the column. The height of the capillary zone was visually estimated by comparing the appearance of the upper part of the column, which contained only residual water, to that of the column just above the piezometric level, which contained capillary water.

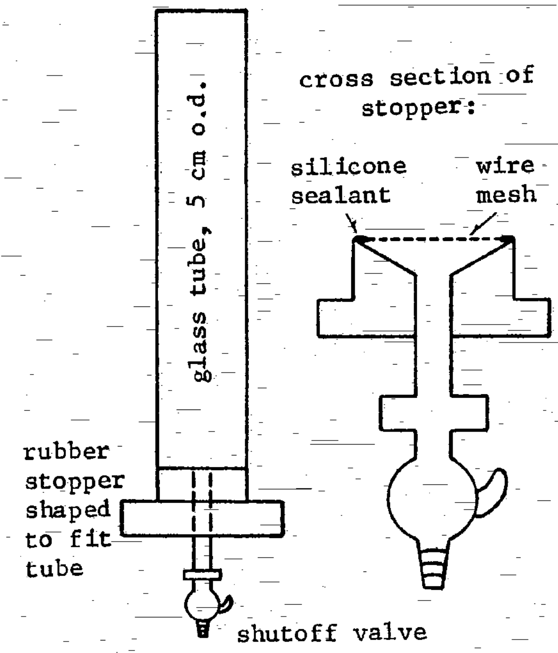
IV. SIEVE ANALYSIS

Particle size distribution was determined by shaking a dry, weighed sample of sand through a series of sieves. Mesh sizes used were 5, 10, 20, 35, 50, and 100. Each sieve was shaken for 10 min. The weight of sand collected by each sieve was then measured. The results are reported as weight percent of sample passing each sieve.

V. SAND COLUMNS - Surfactant Adsorption

Sand columns were prepared and surfactant solutions run through them in an attempt to simulate conditions of the tank experiment on a small scale.

A. Preparation



Columns were constructed as shown at left. The stopper could be removed to facilitate the rinsing out and cleaning of the tube. To pack the column, sand was poured in a steady stream into the tube, which had some DI water already in it. The height of the water was one-third to one-half the desired height of the sand. Once the sand had completely taken up the water, a vibrator was used to pack it more efficiently, starting at the bottom of the column and working up. (This process should be repeated in 2 ft sections if the sand in the column will be higher than 2 ft.) DI water was then run through the column until it came out clear. The water was allowed to drain to the desired level (simulating water table plus capillary zone) and surfactant solutions were added.

B. Initial Experiments

The columns used for the first series of experiments were 4 ft long, but they proved difficult to pack properly and time consuming to run. One experiment with a 4 ft column was completed so that the results could be compared to those from the shorter columns used subsequently.

Pore volumes were calculated by assuming that well packed sand has a pore volume of 33%. Once the water in the column was drained to the desired level, one pore volume of surfactant solution was added at the top. Collection of eluted water started immediately. DI water was added at the top of the column only when the surfactant solution has just disappeared below the top of the sand. The eluted water was collected by pore volume: i.e., for a pore volume of 250 ml, the first 250 ml eluted was stored separately from the second, and so on, so that each could be analyzed separately. Four or five pore volumes were collected for each experiment.

Sand for these initial experiments was collected from around the model soil/aquifer and sieved through a 2 mm sieve. It contained some organic matter. The data are tabulated below.

It appears that using 15 in. columns instead of 4 ft columns did not change the results significantly. The difference in the amount of YLA eluted from columns 3 and 4 is probably due to the fact that the PE-90 in column 4 put YLA into solution. The YLA solution from column 3 was very cloudy; perhaps micelle formation limited the sand-YLA interaction, lowering the chances for adsorption.

Column	Pore Volume	Surfactant Conc. (ppm)	Total Surfactant(g)	% of Surfactant added	Result
1	PV_1	732	0.497	4	65% eluted 4 ft column 2% PE-90
	PV_2	11,300	7.46	57	
	PV_3	530	0.350	3	
	PV_4	143	0.095	1	
2	PV_1	411	0.095	2	71% eluted 15 in. column 2% PE-90
	PV_2	12,300	2.83	62	
	PV_3	960	0.221	5	
	PV_4	246	0.057	1	
	PV_5	128	0.029	0.6	

Column	Pore Volume	Surfactant Conc.	Total Surfactant(g)	% of Surfactant added	Result
3	PV_1	11	0.0025	0.05	88% eluted 15 in. column 2% YLA
	PV_2	15,500	3.6	78	
	PV_3	1,600	0.368	8	
	PV_4	320	0.074	1.6	
	PV_5	0.8	0.0002	0.005	
4	PV_1	12	0.0027	0.06	
	PV_2	12,250	2.8	61	68% eluted 15 in. column 2% PE-90 & 2% YLA (YLA analyzed)
	PV_3	1,200	0.276	6	
	PV_4	170	0.039	0.9	
	PV_5	14	0.003	0.07	

6500—6 85—3C