EPA-R2-72-110
DECEMBER 1972

Environmental Protection Technology Series

# Oily Waste Disposal by Soil Cultivation Process

Office of Research and Monitoring

U.S. Environmental Protection Agency

Washington, D.C. 20460

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EPA-R2-72-110
December 1972

# OILY WASTE DISPOSAL

# BY SOIL CULTIVATION PROCESS

By

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Project 12050 EZG

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U.S. ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

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Washington, D.C., 20402 - Price $2

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## ABSTRACT

Disposal of oily sludges by utilizing soil microorganisms to decompose the oil has been demonstrated at prevailing soil and climatic conditions at Deer Park, Texas. The oil decomposition rate was about 0.5 lbs/$ft^3$ of soil per month without fertilizers and about 1.0 lb/$ft^3$/month when fertilized. The rate of 1.0 lb/$ft^3$/month is about 70 bbls/acre/month using the upper 0.5 foot of soil. Costs of the soil disposal method, including fertilizers, were about $7.00/bbl of oil and $3.00/bbl of sludge containing 33 percent oil. Major microbiological species active in the soil were members of the genus Arthrobacter, Corynebacterium, Flavobacterium, Nocardia, and Pseudomonas.

Differences in decomposition rate and microbial species due to hydrocarbon type as present in crude, bunker C, and waxy raffinate oils were minimal.

Infrared and gas chromatography examinations of oil extracted from fertilized and unfertilized soils showed differences in organic acid contents and boiling ranges.

Oil and fertilizer chemicals did not infiltrate vertically into the soil at the test location under prevailing conditions.

Rainfall runoff water contained 1) up to 100 ppm extractable oils found to be naphthenic acids and 2) up to 150 mg/l ammonia as N when the nutrients were excessive in the soil.



This report was submitted in fulfillment of Project Number 12050 EZG, under the (partial) sponsorship of the Office of Research and Monitoring, Environmental Protection Agency.

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# SECTION I

## CONCLUSIONS

1. Disposal of oily sludges (hydrocarbon) by microbial action in cultivated soil has been demonstrated at prevailing soil and climatic conditions at Deer Park, Texas.

2. Three simultaneous experiments with three oils, i.e., crude oil, bunker C fuel oil, and waxy raffinate oil, indicated decomposition rates for the three oils to be approximately equal and averaged about 0.5 pounds of oil per cubic foot per month without adding nitrogen and phosphorus nutrients and about 1.0 pound per cubic foot per month when fertilizers were added. This is equivalent to about 70 barrels of oil per acre per month.

3. Cost of the soil cultivation process based on the demonstration project expenses and a disposal rate of 70 barrels of oil per acre was $7.00 per barrel of oil. Assuming oily sludges and waste materials contain 33 percent oil, the disposal cost by the soil cultivation process would be about $3.00 per barrel.

4. An optimum fertilization program appears to be a) the initial addition of chemicals, if needed based upon soil test results, to attain a slight excess of nitrogen, potassium, and phosphorus, and b) test at regular intervals, once per month, for ammonia and nitrate contents of the soil and add small dosages of ammonium nitrate as needed to maintain a positive test result (10-50 ppm) for ammonium and/or nitrate contents.

5. The major species of microorganisms present are members of the genus Pseudomonas, Flavobacterium, Nocardia, Corynebacterium, and Arthrobacter. The nature of the hydrocarbon substrate did not appear to influence the type of organisms present but did affect the number of bacteria in the soil. Crude oil tank bottoms produced the highest count, waxy raffinate oil produced an intermediate count, while bunker C fuel oil exhibited the lowest microbial population. Temperature appeared to have no effect upon the microbial count and distribution. Addition of fertilizer did not affect the microorganism distribution but appeared to be directly related with the total aerobic count.

6. Oil decomposition rates were low when the concentration of oil in the soil approached the starting condition of 10 percent oil in the soil. Also, the low reaction period coincided with the winter months and low temperature period.

7. Both aromatic and saturated hydrocarbons were reduced with time in the soil for crude oil tank bottoms and bunker C fuel oil. Only the saturate fraction of waxy raffinate oil appeared to be reduced

by soil microbial action at conditions existing during the project period.

8. Infrared and gas chromatographic analyses of the oil added to and extracted from soil indicated a) the absence of organic acids in oils added to the soil and the presence of organic acids in each of the extracted oils (oils from plots that were fertilized showed higher concentrations of organic acids), b) the organic acid increase coincided with a decrease in total saturates, and c) the percent weight boiling less than 500°C generally was lower for the oil extracted from the soil at the finish of the project than for either the oil added to or the oil extracted from the soil at the start of the project (the lowest percent weight boiling up to 500°C was extracted from soil which had received the largest quantity of fertilizer materials).

9. Oil and fertilizer chemicals did not infiltrate vertically into the soil at the test location and condition.

10. Rainfall runoff water contained 30 to 100 ppm oil. This oil appeared to be essentially naphthenic acids based upon infrared inspection of oil fractions. Also, rainfall runoff water contained ammonia (nitrogen nutrient) approximately proportional to the excess ammonia content of the soil. Phosphorus and nitrates were not found in runoff water.

11. Oil and nutrient contents of rainfall runoff water from the soil cultivation process can be relatively high, and this discharge water should receive treatment before entering public waterways.

## SECTION II

## RECOMMENDATIONS

This project demonstrated that soil microorganisms decompose petroleum oily waste and that oil and fertilizer chemicals did not penetrate the soil at the location and conditions of the test. However, numerous factors are left unresolved and future experiments should gain knowledge concerning the following uncertainties:

1. The residual oil in the soil after the 18-month project contained organic acids, and those soluble in rainfall runoff water were primarily naphthenic acids. Since most organic acids are water soluble, this suggests that naphthenic acids do not decompose in the soil as rapidly as aliphatic acids or that naphthenic acids are formed from aliphatic or aromatic materials at the soil conditions. Speculatively, large concentrations of naphthenic acids may inhibit microbial growth in the soil, and water washing of these organic acids from the soil to a separate biotreatment system might improve the oil decomposition rate in the soil.

2. Residual oil extracted from the soil was characterized by infrared to be polyaromatic oils, suggesting this hydrocarbon group to be slow reaction or nonreactive for microbial decomposition at the prevailing conditions. Certain, and yet unknown, environmental conditions might improve the decomposition rate of the polyaromatics.

3. Accumulation and buildup of metals or salts contents with long-range usage perhaps affects the microorganism activity. The acidity or alkalinity range, optimum for microbial action, may vary with the soil contents.

For application of the process, the following items must be considered:

1. The time required for native soil bacteria to become acclimated oil decomposers likely depends upon the soil composition and temperature.

2. Since soil profiles vary, the oil penetration rate into soil needs to be determined at the location where the process is to be used.

## SECTION III

## INTRODUCTION

Petroleum crude oil, fuels, and lubricants become waste components when emulsified with water, solids, and/or debris and are potential contaminants of surface and subsurface waters. The volume of oily waste is potentially large due to large quantities of petroleum oils handled and used. Sources of the waste are from spillage of crude oil and refined products and from petroleum refinery operations. This paper deals with the refinery operation, but the findings are expected to be applicable for most petroleum sludges.

When large quantities of oil are accidentally spilled on seawater, inland water, or land, much of the oil can often be recovered, but some emulsified waste oils are formed. Removal and disposal of these oily wastes are separate problems for each accident. Also, refining of petroleum crude oil into fuels, solvents, waxes, and asphalts results in small quantities of oily waste materials. These oily sludges obtained on an infrequent basis may be accumulated in a temporary storage vessel or disposed of on a more or less continuous basis. Waste oils from refinery processes and from oil spills are similar in composition.

One method for disposal of oily sludges has been by mixing with the soil and utilizing soil microorganisms to decompose the oil. Application of this method (referred to also as land spreading operation) at several refineries has been reported,[1] and a modification of the method was used during the Santa Barbara oil spill.[2] Wet oil-straw-sand mixture removed from the beaches was disposed of as solid waste in a land fill, and presumably the straw and oil decomposed by microbial action. Many investigations have shown that some microorganisms normally present in the soil will attack petroleum hydrocarbons and utilize them as their sole source of carbon.[3] The reaction is dependent upon many interrelated conditions, which have not yet been fully understood, such as temperature, moisture, soil properties (physical and chemical, including nutrient content), oil content and properties, microbial content, acclimation period, and the availability of oxygen and nutrients. Poorly aerated soils become anaerobic and under these conditions the microorganisms decompose organic matter very slowly. Aeration of the soil by frequent cultivation is a means of supplying oxygen essential for the more rapid acting aerobic microbes.

Although the land spreading or fill method for disposal of oily sludges has been used at some locations, knowledge of the process is limited to a few trial-and-error applications. An exploratory study of hydrocarbon decomposition rates was made by the Shell Oil Company for their disposal area at the Houston, Texas, refinery. Also, spot samples of their soil were analyzed for microorganism contents by

Environmental Protection Agency, National Environmental Research Center, Cincinnati, Ohio. Results of the preliminary hydrocarbon decomposition rate study and microbial counts were reported by Dotson, Dean, Kenner, and Cooke.[1] Sufficient data to permit evaluation of the process were not obtained and are not available from other sources. This paper discusses a further study designed to demonstrate the effectiveness and cost of the soil cultivation process for disposal of oily waste from petroleum.

## SECTION IV

## OILY SLUDGE

Almost all operations of the petroleum industry, including exploring, producing (extracting), storing, transporting, and refining of crude oil and the storing, distributing, and handling of products are potential sources of oily sludges.

Accidental spills of crude oil and petroleum products during the handling, storing, and transporting operations are the principal cause for the formation of oily sludges in large quantities. At refineries, accidents seldom cause oily sludge production. Common sources are incoming crude oil, ship ballast water, tank and vessel cleanings, oil-water separators, and numerous miscellaneous sources such as sewer boxes and emulsion breaking facilities (demulsifier). The quantity of oily sludge for disposal at a refinery does not depend only upon the nature of the crude and processing units. Oily sludge formation can be minimized by prudent operating practices, sensitive attitudes and suitable control methods. Generally, most of the oily sludges accumulate in oil-water separators and in tank bottoms.

Crude oil shipped to the refinery contains emulsified material which is commonly referred to as bulk, sediment, and water (BS&W). The BS&W concentration in the crude oil ranges from about 0.01 to 0.1 percent by volume (%v). This BS&W fraction contains about 30%v oil, 50%v water, 10%v carbonaceous matter, and inorganic salts equivalent to about 10%v. The carbonaceous material which is the part of BS&W that could eventually become oily sludge for disposal, amounts to about 0.005 percent of the incoming crude oil to the refinery. However, in the refining steps, much of this carbonaceous material is utilized into fuels. The quantity of waste sludge from crude oil is small for the following reasons: 1) Crude oil receipts at a refinery are often stored in tanks for a few days before being fed to processing units. During quiescent periods, most of the BS&W material settles out as tank bottoms and is removed during tank cleanings at three to five-year intervals. Fortunately, tank bottoms have been in demand for oil and wax recoveries by independent operators and for road bed additives. When crude tank bottoms must be handled at the refinery, a concentration step is possible with conventional slop oil demulsifying facilities. The BS&W emulsion is broken and some of the carbonaceous material is included with the recovered oil phase and some with the water phase. The recovered oil phase is fed to a refining unit and the water phase flows into an oil-water separator. 2) In the event a settling time is not possible, the crude oil containing BS&W material is fed to a crude distilling unit. The BS&W material is removed in the pretreatment (heater and desalter) section of the distilling unit. The oil fraction of the BS&W remains in the crude. Water fraction in the desalter effluent flows into the feedwater stream of an oil-water separator. Emulsified materials in the oil-water separator will either

enter the recovered oil stream, settle with the bottom sludge inside the separator box, or remain in the water phase flowing to secondary treating facilities.

Ship ballast water-handling facilities vary at different refineries as does the quantity and quality of both the water and oil phases of the incoming ballast water. At Shell Oil Company's Houston Refinery, ballast water from docked ships is pumped into an American Petroleum Institute (API) design ballast tank, and the water drained from this ballast tank flows by gravity into a holding pond equipped with downstream oil retention baffles and skimmers. Incoming ballast water sometimes contains oily material which has a density near that of water and will pass through the ballast tank into the holding pond. If heavy oil or emulsion material remains in the holding pond for a few days, the physical characteristics change from a fluid brownish-black mixture to a thick congealed mass (sometimes greenish in color) which will float on the water but will not flow. This change apparently is caused by microorganisms. The congealed mass containing oil may be treated in a demulsifying unit to recover the oil. If judged to be low in oil content, it may become a part of the oily sludge which is a potential feed for the soil cultivation process. The frequency and quality of oily waste from the ship ballast water source are uncontrolled and unknown.

Tank bottoms obtained during cleaning of tanks vary in composition and the residual oil content can usually be recovered or at least reduced with emulsion breaking facilities. However, the real bottoms and final washings from a tank are often oily sludges not suitable for feed to a demulsifier unit and are potential feed for the soil cultivation process.

Oily sludge from oil-water separator and holding pond cleanings is usually low in oil content and is suitable for disposal by means such as the cultivation process. The sludge cleanings from the water box or pond usually contains about two percent carbonaceous material. Oil box cleanings which are mostly oil can be fed to the demulsifying unit, but sometimes mixtures of oil, straw, grass, and dirt make this material suitable only for disposal.

Solids and oily waste at the demulsifying unit usually accumulate in tanks which must be cleaned occasionally, and these cleanings cannot be further improved with additional treatment in demulsification facilities. Disposal of this oily-sand material can be accomplished by the soil cultivation process.

Process unit shutdowns include complete cleaning of a piece of equipment and/or vessel before maintenance work begins. In the shutting down of a process unit, oil is returned to storage. Immediately after shutdown and where possible, the equipment is washed with water which removes residual traces of oil and carbonaceous material. This material is sent to an oil sewer which connects to an oil-water separator.

## SECTION V

## PROJECT DESCRIPTION AND OBJECTIVES

The soil cultivation process consists of the treatment of oily waste material by spreading and cultivating into soil under prevailing climatic conditions. The project includes three parallel experiments. Oily feed materials were selected to represent different combinations of hydrocarbon types. These were designated as sludge A, sludge B, and sludge C.

Sludge A was a crude oil tank bottoms which contained a natural balance of hydrocarbon types.

Sludge B was a high molecular weight fuel oil (bunker C or No. 6) containing olefinic and aromatic components.

Sludge C was a waxy raffinate, which is an intermediate waxy oil product containing highly paraffinic components.

The properties of the three oily materials (simulated sludges) used in the study are given in Appendix A. Sludge A was added to each of the three separate soil test plots designated A-1, A-2, and A-3. These test plots were treated identically except for soil nutrient additions. A-1 was fertilized heavily, A-2 received a moderate or intermediate quantity of fertilizer material, and A-3 was the control with zero addition of fertilizer. Sludge B was added to three separate plots also, and these were designated B-1, B-2, and B-3. Likewise for sludge C, experimental plots were C-1, C-2, and C-3. Again, the No. 1 plots were fertilized heavily, No. 2 plots received intermediate quantity of fertilizers, and No. 3 plots were not fertilized. The design and details of the project are discussed separately.

Objectives of the project were to determine:

1. The decomposition rate of oily waste sludges in cultivated soil.

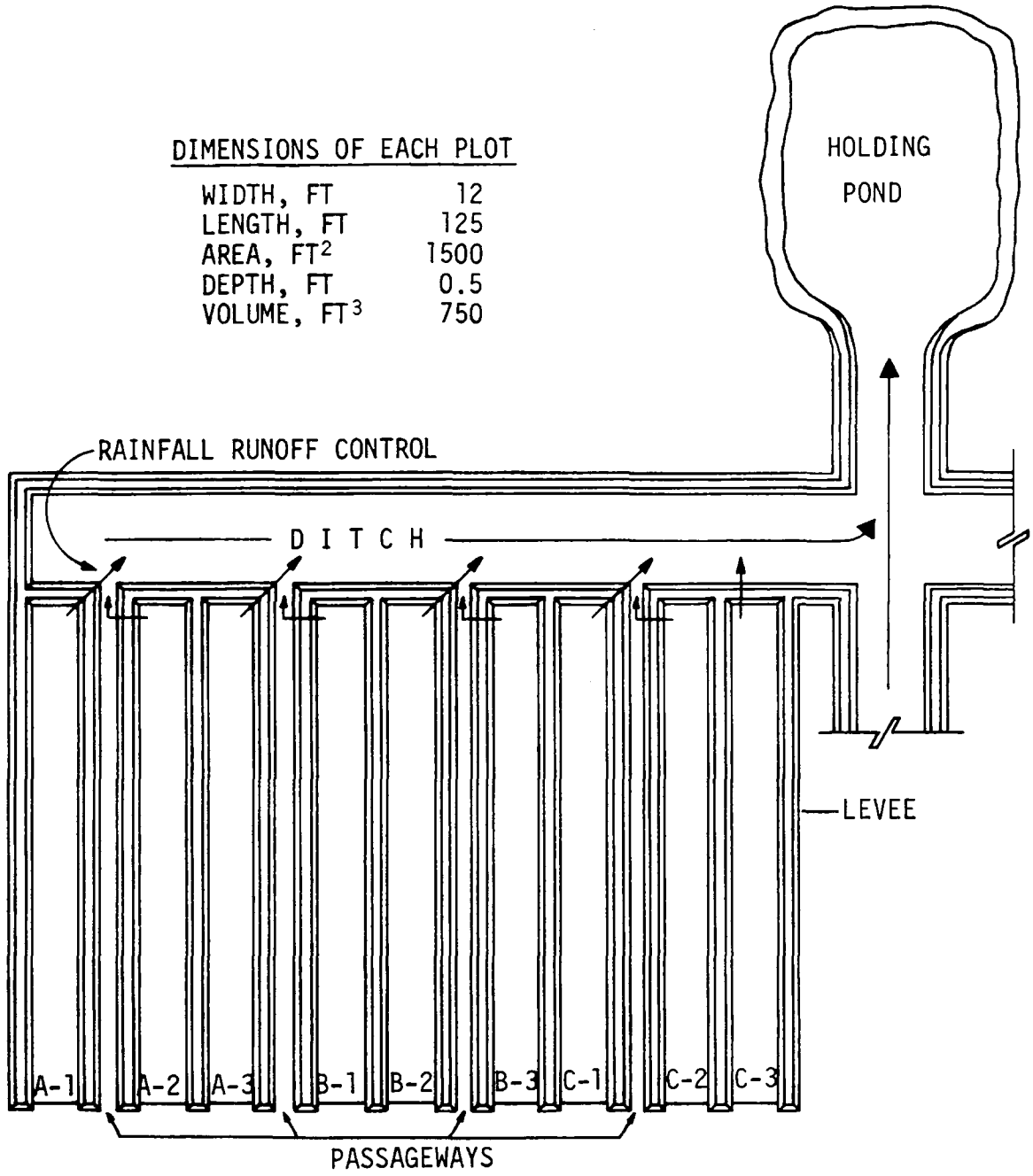
2. The effectiveness of adding nutrient supplements.

3. Major microbiological species active in soil where oily wastes are decomposed.

4. The cost of the process for disposal of oily waste.

5. If the oil infiltrates vertically into the soil at the test site and the depth of penetration.

FIGURE 1




EXPERIMENTAL PLOTS

## SECTION VI

## SOIL TEST PLOTS

Nine soil test plot areas were needed to conduct three parallel experiments with sludges A, B, and C. The layout of plots A-1, A-2, A-3, B-1, B-2, B-3, C-1, C-2, and C-3 is shown in Figure 1. Each of the nine plots was 12 feet in width and 125 feet in length (1500 square foot area). The plots were located near the Houston Ship Channel within the Shell Oil Company refinery at Deer Park, Texas.

The plots were separated by levees and were designed so that rainfall runoff from each plot drained through a pipe to a ditch. A plug in the pipe was used to control the runoff. The levees prevented crossflow of water from one plot to another and kept oil within the plot area. Excess runoff water flowed from the ditch into a holding pond (Figure 1) and was either discharged to the Ship Channel or transferred by vacuum truck to the refinery biological treating facilities.

Space between the plots permitted tank truck passageway adjacent to each plot for convenience in spreading oily sludge evenly over the surface. Also, the plots were cultivated separately. Before moving from one plot to another, the space between plots was cultivated to clean the plow and prevent mixing of oil, soil, and fertilizers from one plot to another.

The experimental plots are located in an area which had been used previously for oily waste disposal. This offered the advantage of having a start of oil-consuming variety of microorganisms in the soil without an acclimation period. However, a disturbing disadvantage as far as the experimental work was concerned was the presence of residual oil in the soil at the start of the experiment. Initial leveling and grading of the area and preparation of the levees to separate each plot area are shown in Figure 2. Identification markers were installed as shown in Figure 3.

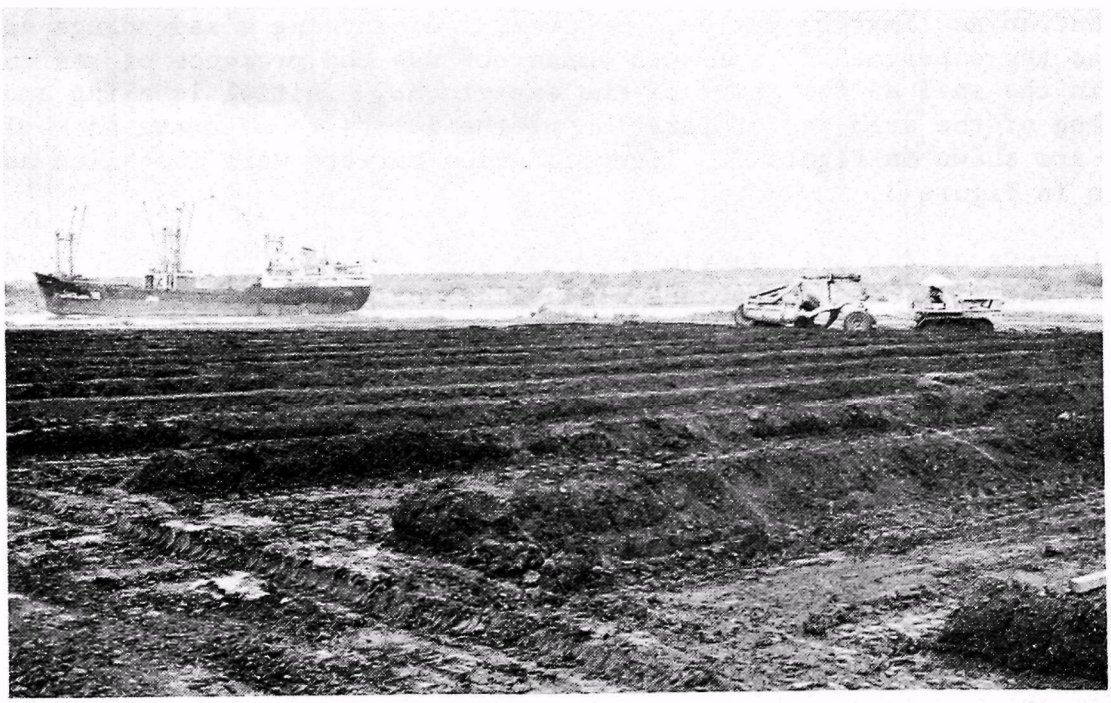
The texture of top soil sample from the plot area was 58 percent sand, 14 percent silt, and 28 percent clay. The soil textural classification was sandy clay loam. At a depth of two feet from the surface, the soil was classified as loam and at four-foot depth was sand.

The bulk density of oil-free top soil was 1.6 or equivalent to approximately 100 pounds per cubic foot. The cation exchange capacity at the start was about 10 milliequivalents per 100 grams (me/100g) of soil and at the end of the experiment ranged from 30 to 60 me/100g. (This increase in exchange capacity is larger than expected from the effects of adding fertilizers and oil materials. The sample taken at the start of the project may not have been representative as the samples at the close of the experiment.) Conductivity was 13 micromhos per centimeter (Mmhos/cm) at the beginning and ranged from about 4 to 6 Mmhos/cm at

FIGURE 2

PREPARATION OF TEST PLOTS

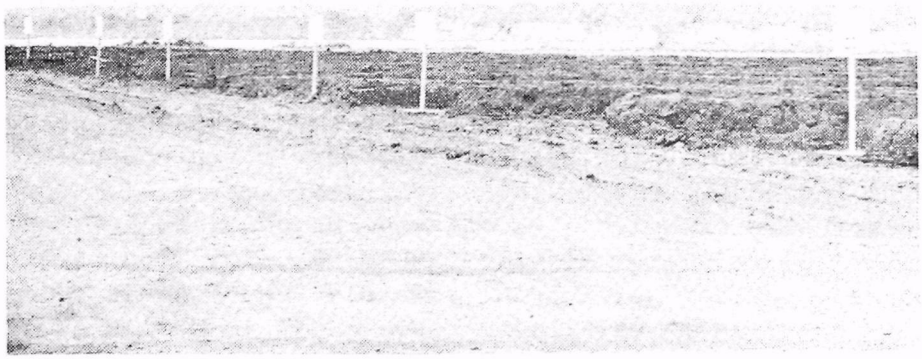
LEVELING AND GRADING



PREPARATION OF LEVEES TO SEPARATE PLOT AREAS

FIGURE 3

SOIL PLOT IDENTIFICATION MARKERS



SIGN AT PROJECT SITE


IDENTIFICATION MARKER FOR EACH PLOT

the close of the study. Conductivity measurements were made at room temperature (20-22$^{o}$C). Other properties (including pH, oil, nitrogen, phosphorus, sulfur and metals contents) of the soil at the beginning of the project are tabulated and discussed along with results of the study.

## SECTION VII

## SOIL NUTRIENTS (FERTILIZER)

Since the disposal of oily waste by the soil cultivation process depends upon the soil microorganisms to oxidize the oils or convert the oily waste into cell protoplasm, the ingredients needed for microbial growth must be present. The main elements are carbon, hydrogen, oxygen, nitrogen, potassium, and phosphorus. Also, key trace elements including sulfur, sodium, calcium, magnesium, iron, and others are needed. Most of the trace elements are abundant in soils, but two of the main elements, nitrogen and phosphorus, often limit organic cellular growth. Chemical analyses of protoplasm indicate phosphorus requirement is about one-fifth the nitrogen requirement.[4]

In agricultural crop production, nitrogen and phosphorus are removed from the soil with the harvested grain or forage. Replenishing of the nutrients is required. For a waste disposal system such as the soil cultivation process, there should be an equilibrium condition established which would minimize the need for supplementing the nutrients. Endogenous metabolism, autoxidation of cellular protoplasm, results in the release of nitrogen and phosphorus previously used for synthesis. The released nutrients are made available for reuse in biological waste treatment systems.[4] No reference information was found to use as a guide in selection of appropriate quantities of nitrogen and phosphorus which should be added to the biological system. Instead, the selection of fertilizer quantities was based upon agricultural-oriented experience. Grass land is frequently fertilized with 500 pounds of nitrogen and 100 pounds of phosphorus per acre, and three times these quantities have been used according to our consultants. Warnings that 1) excess nitrogen fertilizer elements hinder (poison) bacterial action and 2) excessive total soluble salts may cause unfavorable osmotic conditions for bacterial growth, were considered in the selection of the quantities of nutrient additive. Excess phosphate was not considered toxic except for its contribution to the total soluble salt content. Initial additions in pounds per acre (lbs/ac) of nitrogen (urea) as N were 1000, 500, and zero to plots 1, 2, and 3, respectively. The additions of phosphorus (calcium hydrogen phosphate) were 200, 100, and zero lbs/ac as $P_2O_5$ to plots 1, 2, and 3, respectively.

Periodic analyses of nitrogen and phosphorus were made, and additional fertilizer materials were added to plots 1 and 2 during the course of the experiment. The types and quantities of fertilizer materials added during the study are shown in Table 1.

TABLE 1

NUTRIENTS ADDED DURING THE STUDY
(The Number 3 Plots Were Not Fertilized)

| FERTILIZER | RATIO N-P-K | | 1970 MAY 7 PLOTS NO. 1 | 1970 MAY 7 PLOTS NO. 2 | 1970 AUGUST 7 PLOTS NO. 1 | 1970 AUGUST 7 PLOTS NO. 2 | 1971 JAN. 27 PLOTS NO. 1 | 1971 JAN. 27 PLOTS NO. 2 | 1971 APRIL 21 PLOTS NO. 1 | 1971 APRIL 21 PLOTS NO. 2 | 1971 AUGUST 11 PLOTS NO. 1 | 1971 AUGUST 11 PLOTS NO. 2 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Urea, as N | 45-0-0 | lb/plot | 34 | 17 | 58 | 23 | | | | | | |
| | | lb/acre | 1000 | 500 | 1700 | 680 | | | | | | |
| | | ppm by wt | 450 | 225 | 775 | 305 | | | | | | |
| Ammonium Nitrate, as N | 35-0-0 | lb/plot | | | | | 35 | 17 | 9 | 4.5 | 12 | 6 |
| | | lb/acre | | | | | 1000 | 500 | 260 | 130 | 350 | 175 |
| | | ppm by wt | | | | | 470 | 225 | 120 | 60 | 160 | 80 |
| Phosphorus, as $P_2O_5$ | 0-46-0 | lb/plot | 7 | 3.5 | 184 | 46 | | | | | | |
| | | lb/acre | 200 | 100 | 5350 | 1340 | | | | | | |
| | | ppm by wt | 95 | 47 | 2450 | 610 | | | | | | |
| Potash, as $K_2O$ | 0-0-60 | lb/plot | | | | | 30 | 15 | | | | |
| | | lb/acre | | | | | 875 | 438 | | | | |
| | | ppm by wt | | | | | 400 | 200 | | | | |

## SECTION VIII

## STARTUP, OPERATION, AND APPEARANCE

After the plots had been laid out and the levees prepared, each plot was cultivated with a "roto-tiller" type plow. Fertilizer materials were added by manually spreading the solid granular fertilizer over the surface of plots No. 1 and 2. After spreading fertilizer and before adding oily sludge materials, the plots were cultivated a second time to mix and distribute the fertilizer salts with the soil.

Simulated oily sludges were transported to the test plot area with a vacuum tank truck, and the sludge was distributed over the surface of the soil by manual direction of a discharge hose attached to the tank. Soil cultivation and addition of oil are shown in Figure 4. Mixing of the oil and the soil by cultivation appeared uniform and presented no problem at the ambient May temperature of about 80°F.

The initial schedule for cultivating the soil plots was once each two weeks, weather permitting. However, after the first quarter, the plowing frequency was increased in an attempt to improve oil decomposition rates. The plowing frequencies and results are discussed separately. After about six months of cultivation, the soil was friable, had lost the oily appearance, and was judged from test results to be suitable for a second addition of the oily sludge. Some differences in the plots were obvious. For instance, the color of the No. 3 plots was darker than that for Nos. 1 and 2. Photographs of these plots just before and just after the addition of the second application of the simulated oily sludges are shown for the "A" plots in Figure 5, for the "B" plots in Figure 6, and for the "C" plots in Figure 7. The date for this second addition of sludge was in early February, and the temperature was in the low 40's °F. Congealing and solidification of the sludges were apparent, and mixing of the viscous oily matter into the soil was not successful until the ambient temperature had increased to about 80°F.

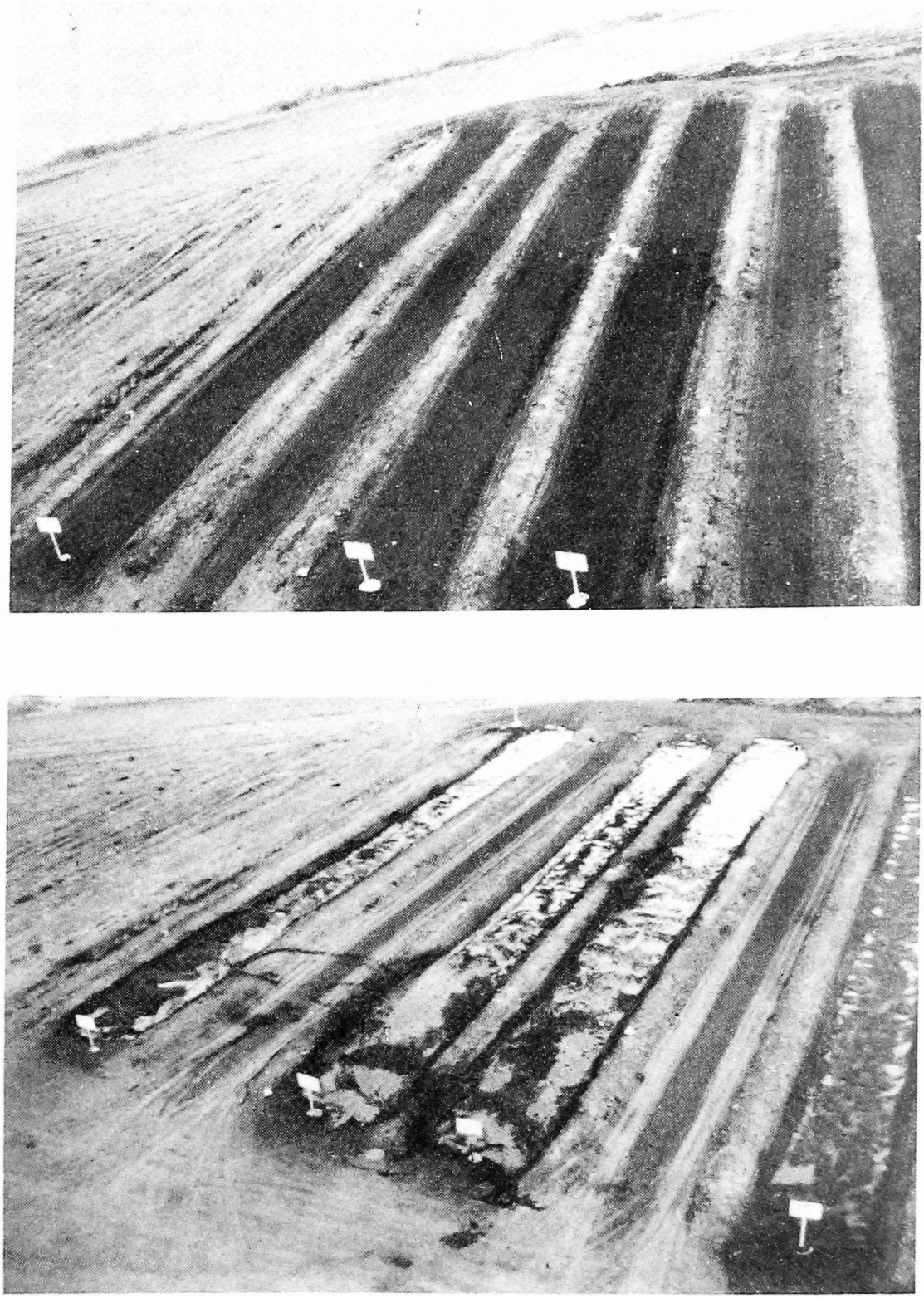
At the close of the 18-month experiment, the soil had again returned to a friable condition with the appearance of a normal agricultural soil. A close-up view of soil in plots A-1, B-1, and C-1 is shown in Figure 8.

Although no attempt was made to grow vegetation matter on soils previously used for oil decomposition during this experiment, native grass and plants did sprout and grow on top of the levee. The soil in the levees was the same as the starting test plots, which contained about ten percent oily material as discussed later.

FIGURE 4

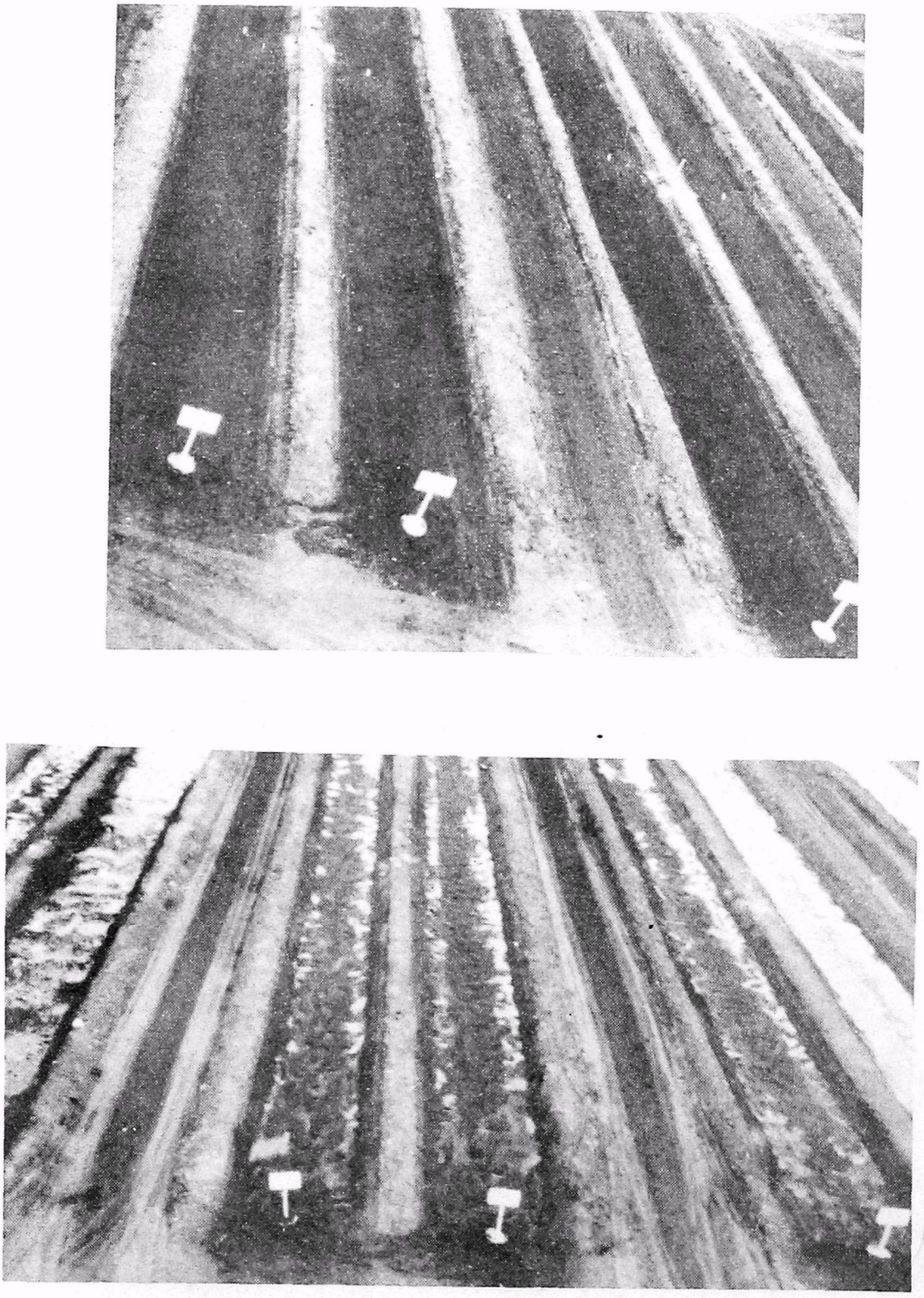
SOIL CULTIVATION AND ADDITION OF OIL

FIGURE 5



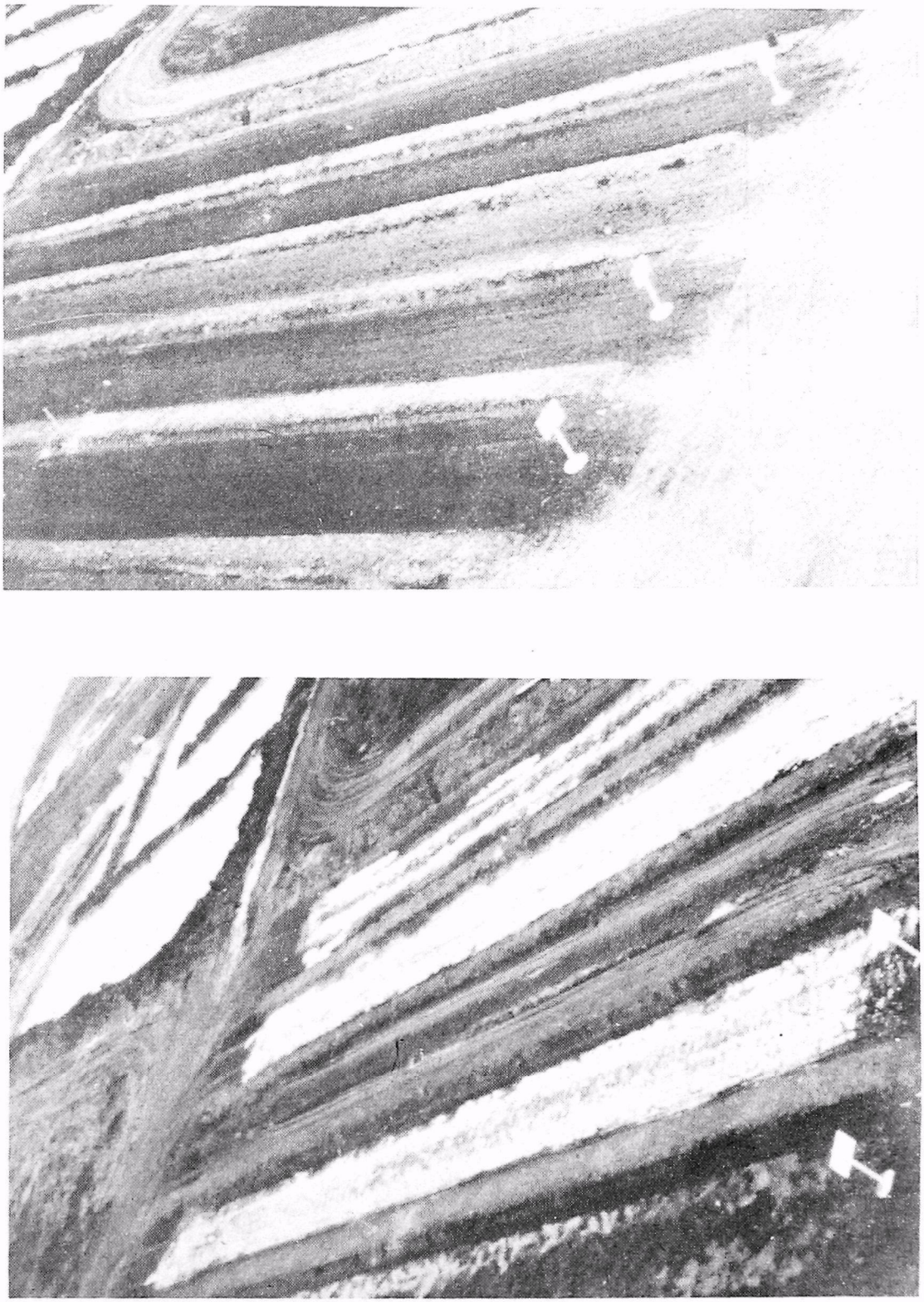
BEFORE AND AFTER SECOND ADDITION OF OIL TO "A" PLOTS

FIGURE 6



BEFORE AND AFTER SECOND ADDITION OF OIL TO "B" PLOTS

FIGURE 7



BEFORE AND AFTER SECOND ADDITION OF OIL TO "C" PLOTS

FIGURE 8

SOIL AT END OF THE DEMONSTRATION PERIOD

## SECTION IX

## SAMPLING AND TESTING

Oil and nutrient contents were used as controls for the experimental work during the 18-month project, and these components were tested frequently. (Microbiological analyses, hydrocarbon types of oil added to and extracted from the soil and the oil content of soil core samples at depths up to six feet were made to achieve the project objectives. Also, metals, nitrogen, phosphorus, and sulfur contents of the soil and infrared absorption and gas chromatography of extracted oils were examined.) The samples for analyses, analytical tests, method references, and the frequency of tests during the experimental period are summarized in Table 2. In addition, moisture, pH and temperature of the soil were measured on a regular basis. Moisture contents of the soil were obtained along with the oil content determinations as described in Appendix E. Temperature and pH were measured using mercury thermometers and a glass-calomel electrode meter. The soluble nutrients were dissolved from oil-free soil (after $CCl_4$ extraction) using distilled deionized water for nitrogen and 1.4 normal (1.4 N) ammonium acetate ($NH_4Ac$) in hydrochloric acid (HCl), pH 4.2, for phosphorus (P), sodium (Na), potassium (K), magnesium (Mg) and calcium (Ca), according to the procedure recommended by State Soil Testing Laboratories publication.[10] For the less soluble metals, zinc (Zn), manganese (Mn), copper (Cu), iron (Fe), and lead (Pb), a 50/50 mixture of concentrated HCl and concentrated nitric acid ($HNO_3$) was used for the extraction solvent. Analyses of the solutions were by atomic absorption. The soil consultant used 1.0 N $NH_4Ac$ at pH 7 for extracting P, K, Na, Ca, and Mg, and 0.1 N HCl for extracting Zn, Mn, Cu, and Fe. These latter extraction solvents are generally considered a good measure of the quantities of elements available for growth of plant life. Rainfall runoff water was tested for oil and nutrient contents. The method used for oil in water determinations was American Petroleum Institute (API) method 731.[14] Oxygen determinations of the soil, although desirable, were not made because a suitable method was not available.

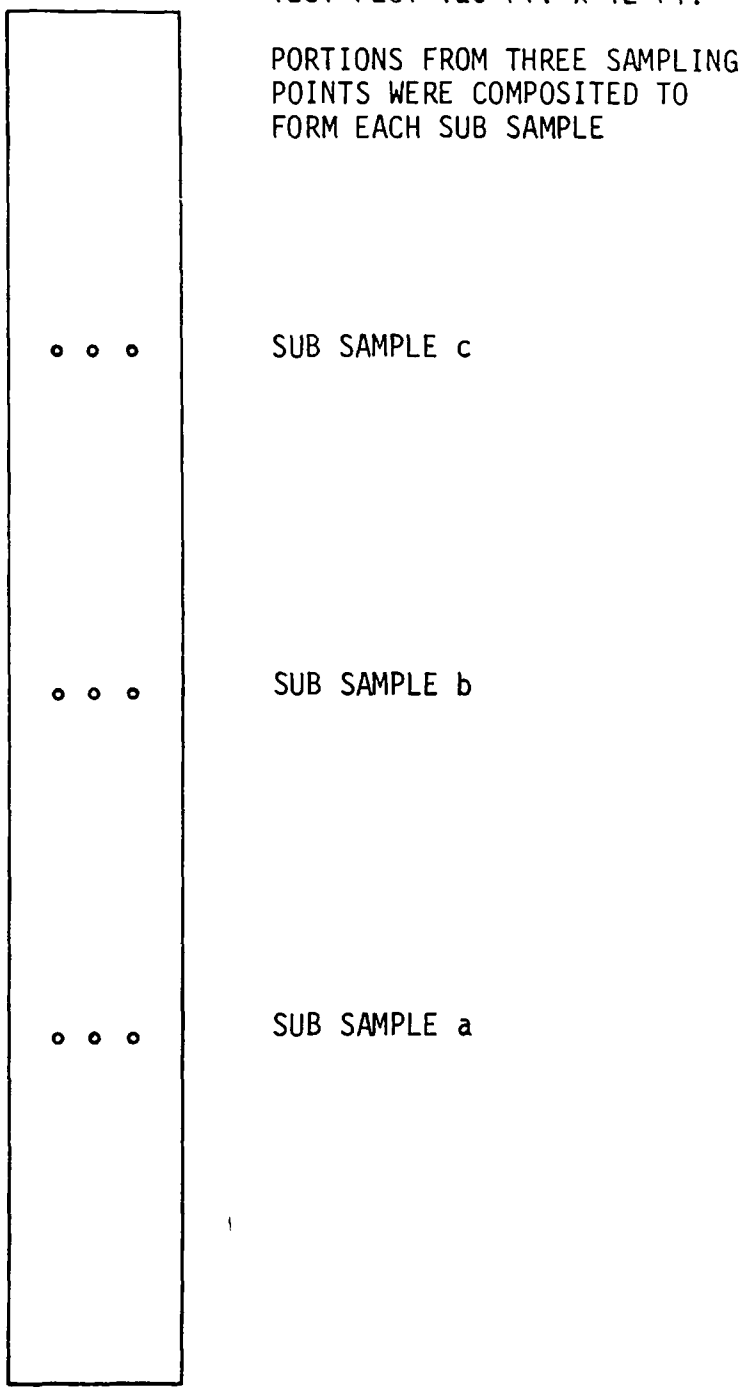
The obtaining of a representative soil sample was a recognized problem from the start of the project. Although cultivation mixed the surface soil vertically, complete horizontal and vertical mixing throughout a test plot was not attained. In an effort to minimize inconsistencies, samples were taken immediately after cultivation and from several locations, then composited before submitting for tests. The sampling procedure included combining portions of soil from three sampling points to form subsamples a, b, and c, as shown in Figure 9. Each subsample was analyzed separately for oil content, and the resulting data for the 18-month experimental period are given in Appendix A. For all other tests, including nutrients, microbial and metals contents, and other properties of the soil, subsamples a, b, and c were

TABLE 2

SAMPLING AND TESTING FREQUENCY

| Sample | Analytical Test | Reference | Approximate Frequency |
|---|---|---|---|
| Soil, top 6 inches | Oil content | Appendix E[8] | Bi-weekly |
| | Nutrients ($NH_3$, $NO_3$, $P_2O_5$) | Standard methods[5,10] | Monthly or bi-weekly if needed |
| | Total nitrogen, phosphorus and sulfur | Specific methods[11,12,13] | Beginning and end |
| | Microbial content | Appendix B[6] | Monthly |
| | Metals | Atomic absorption | Beginning, midway, and end |
| Soil core, 2, 4, & 6 ft. | Oil content | Appendix E[8] | Beginning, midway, and end |
| | Nutrients ($NH_3$, $NO_3$, $P_2O_5$) | Standard methods[5,10] | Midway and end |
| Oil extracted from soil | Hydrocarbon type | ASTM D-2007[9] | Beginning, midway, and end |
| | Infrared spectroscopy | Appendix D | Beginning, midway, and end |
| | Gas chromatography | Shell Oil Co.[7] | Beginning and end |
| Oil added to soil | Physical properties | ASTM methods | Beginning |
| | Metals | Emission Spectroscopy | Beginning |
| | Hydrocarbon type | ASTM D-2007[9] | When added |
| | Total nitrogen, phosphorus and sulfur | Specific methods[11,12,13] | Beginning |
| | Infrared spectroscopy | Appendix D | Beginning |
| | Gas chromatograph | Shell Oil Co.[7] | Beginning |

FIGURE 9




TYPICAL SAMPLING POINTS

composited to represent the whole test plot. For example, A-1 soil sample was a composite of A-1a, A-1b, and A-1c subsamples.

Analytical results are given in Appendices A, B, C, and D.

## SECTION X

## EFFECTIVENESS OF THE SOIL CULTIVATION PROCESS

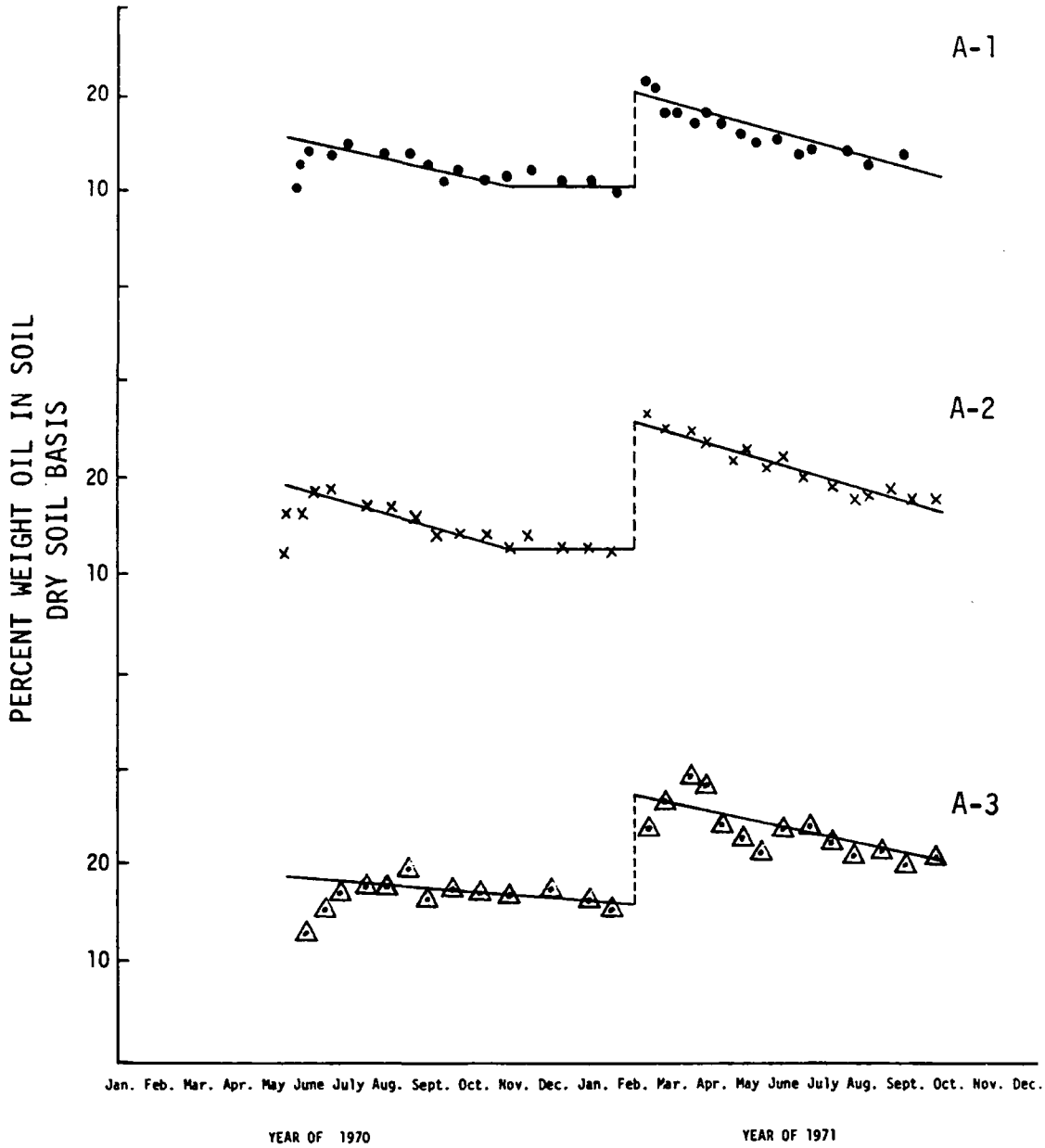
### Oil Decomposition Rate and Effect of Fertilizer

Percent weight oil in each soil plot given in Tables 5, 6, and 7 of Appendix A are shown graphically related with time in Figures 10, 11, and 12. Residual oil of about ten percent in the soil was due to previous use of the soil area for oily waste disposal as mentioned earlier. The increased quantities of oil in all plots for May 1970 and February 1971 were due to the addition of oil to the soil. Deviation in the oil content data from the linear relationships shown on each of the figures may indicate more rapid reaction during some periods than others but is likely due to nonrepresentative samples. The straight line relationship was calculated by the method of least squares. For the "B" plots, Figure 11, inconsistent data during February to April, 1971, were due to the inability to mix the highly viscous oil into cool soil with the roto-tiller type cultivator.

Generally and as shown in each of Figures 10, 11, and 12, from the first addition of oil in May 1970 to about November 1970, the oil content of the soil decreased markedly. During the period November 1970 to February 1971, a reduction of oil was not apparent. From February, when a second dosage of oil was added, to October 1971, the oil content again decreased. The reason (or reasons) for the period of inactivity is not clearly evident. During this period, food supply may have been limiting because the concentration of oil in the soil was in some cases near the starting content, and this residual oil may be nonreactive or slowly reactive with soil microorganisms. Another reason may have been the lack of available nutrients which ranged from about 10 to 50 ppm ammonia as N during this period. A third reason may have been temperatures that were too low for favorable bacterial growth.

The soluble nitrogen (N) and phosphorus (as $P_2O_5$) contents from Table 5 of Appendix A for the "A" plots during the project are shown in Figures 13, 14, and 15. The trend of these nutrient data for the "B" and "C" plots is similar and is not shown graphically. Urea was used as the nitrogen nutrient at the start of the project as recommended by a soil consultant. The reason for selecting urea was to avoid increasing the salt content of the soil. Immediately after fertilizing in May 1970 (Figure 13), the ammonia ($NH_3$) content was about 700 ppm by weight as N in the soil. This was likely due to inadequate mixing or nonrepresentative sample because the theoretical amount added was about 460 ppm as N (Table 1). The concentration rapidly decreased to about 30 ppm as N during June and to zero in July. A larger dosage was added in August causing the $NH_3$ concentration to reach about 1500 ppm as N. During September and October, the $NH_3$ content remained about 500 ppm as N. During this same period, the nitrate ($NO_3$) content was zero and ammonia was being lost to the atmosphere. The odor of ammonia

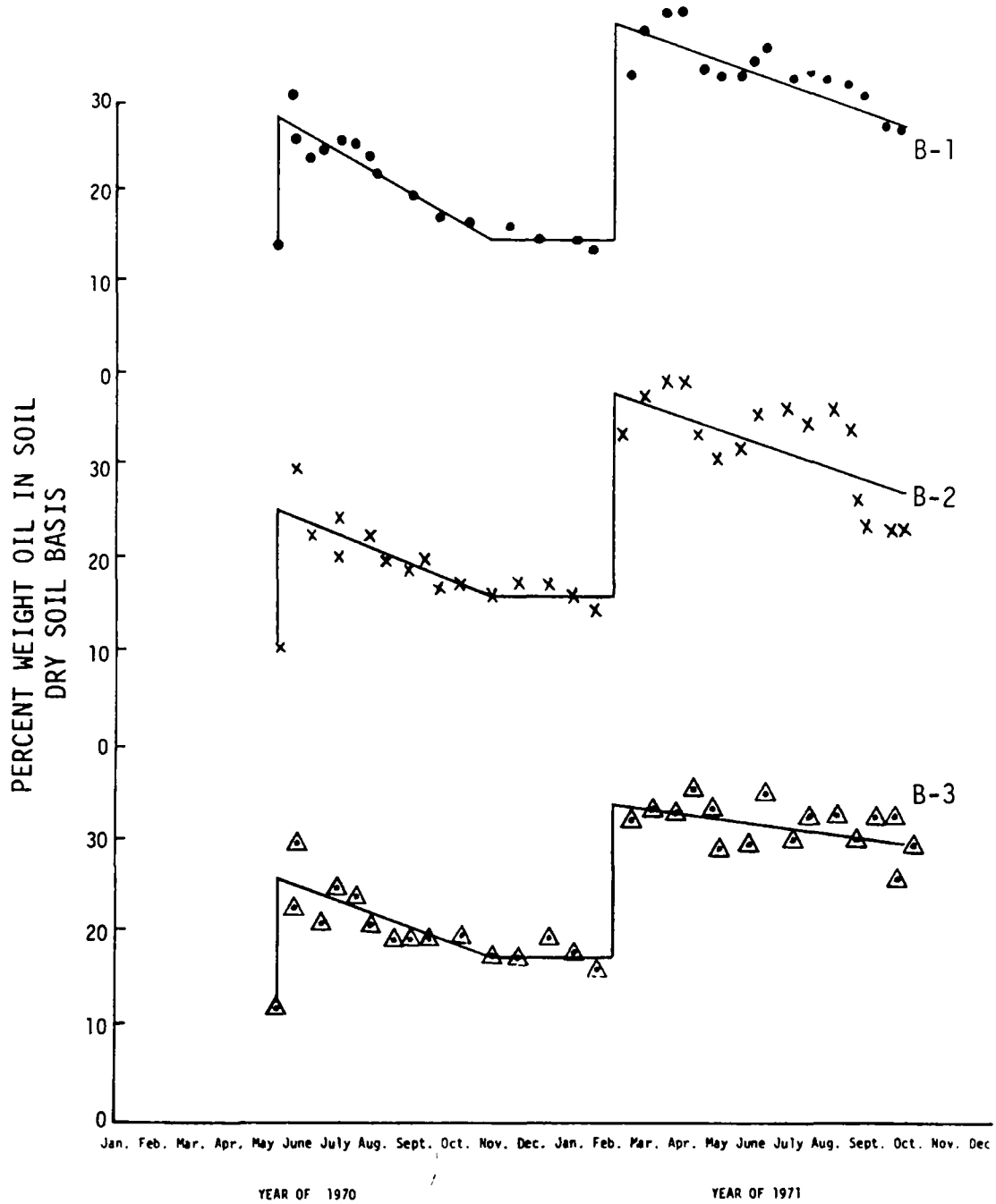
FIGURE 10




OIL CONTENT OF SOIL

"A" PLOTS

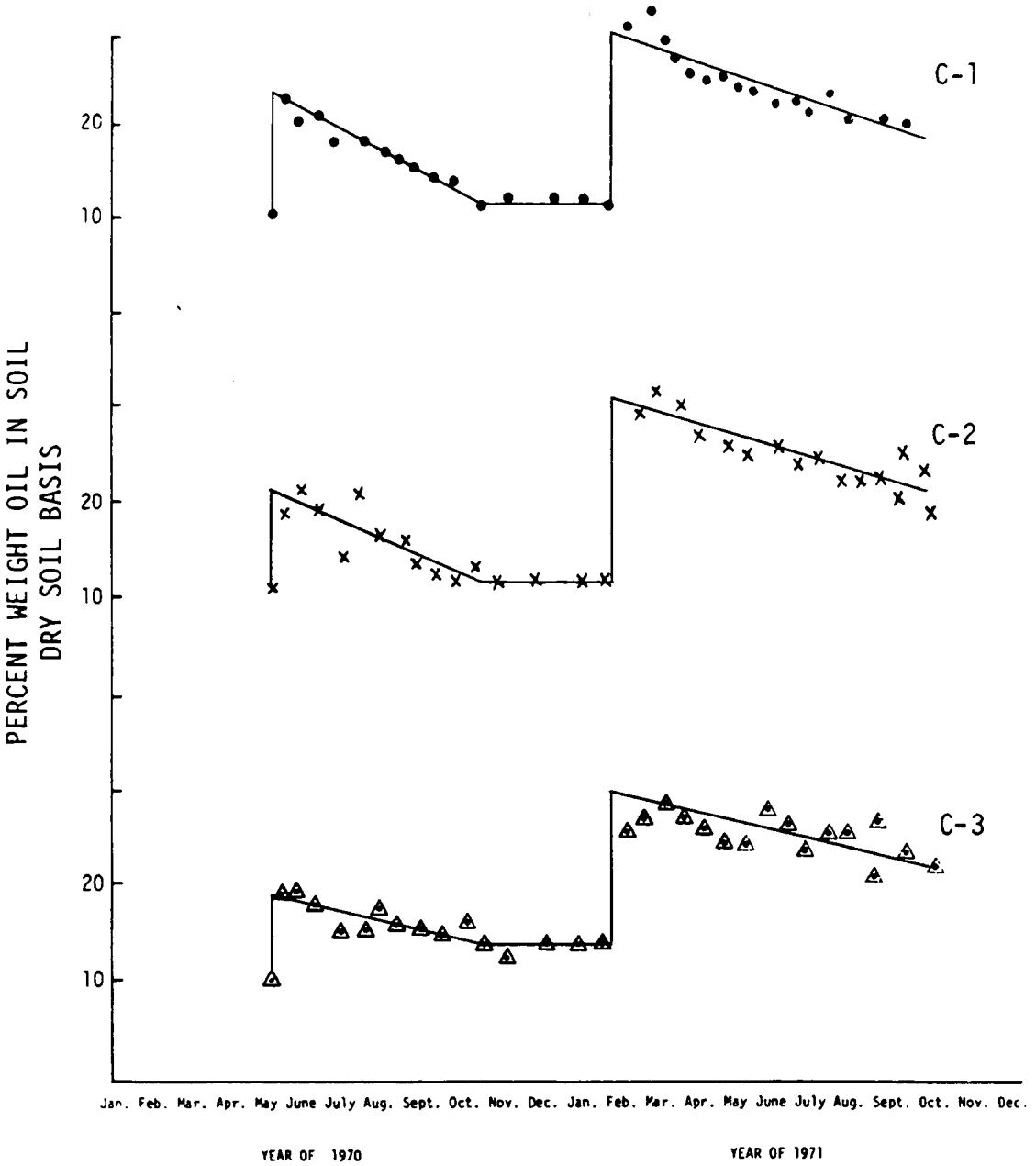
FIGURE 11




OIL CONTENT OF SOIL

"B" PLOTS

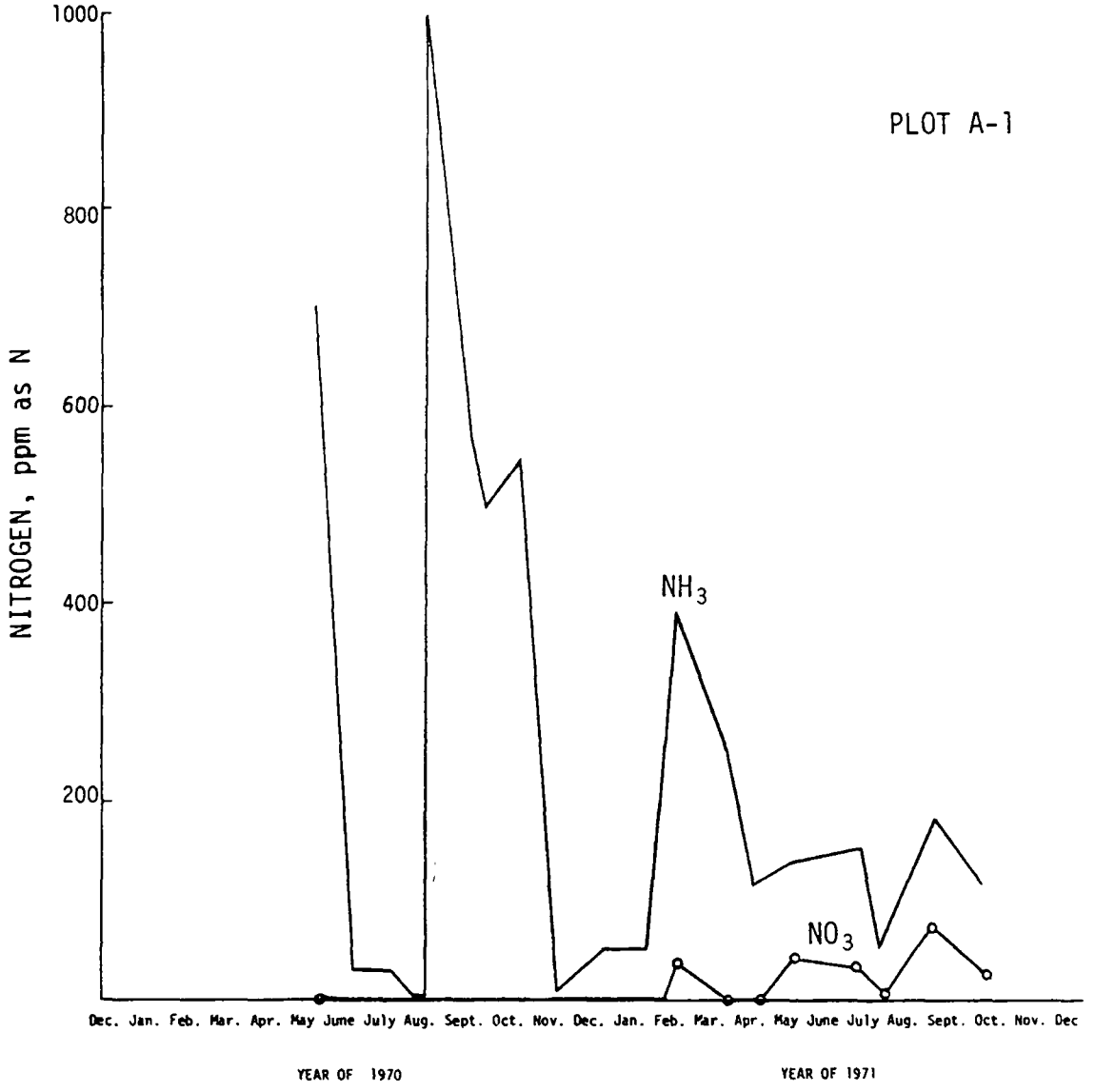
FIGURE 12




OIL CONTENT OF SOIL

"C" PLOTS

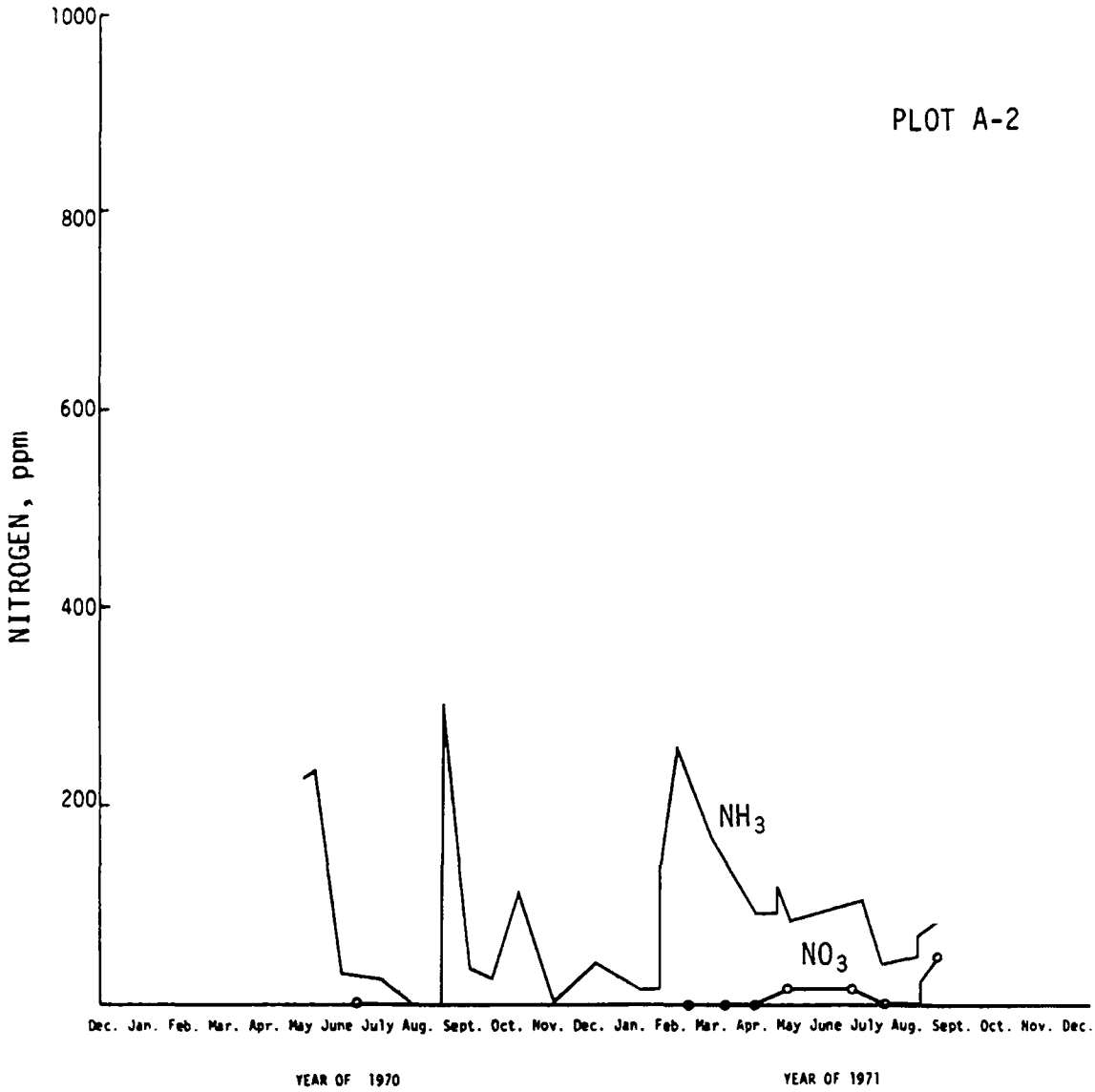
FIGURE 13




NITROGEN CONTENT OF SOIL

PLOT A-1

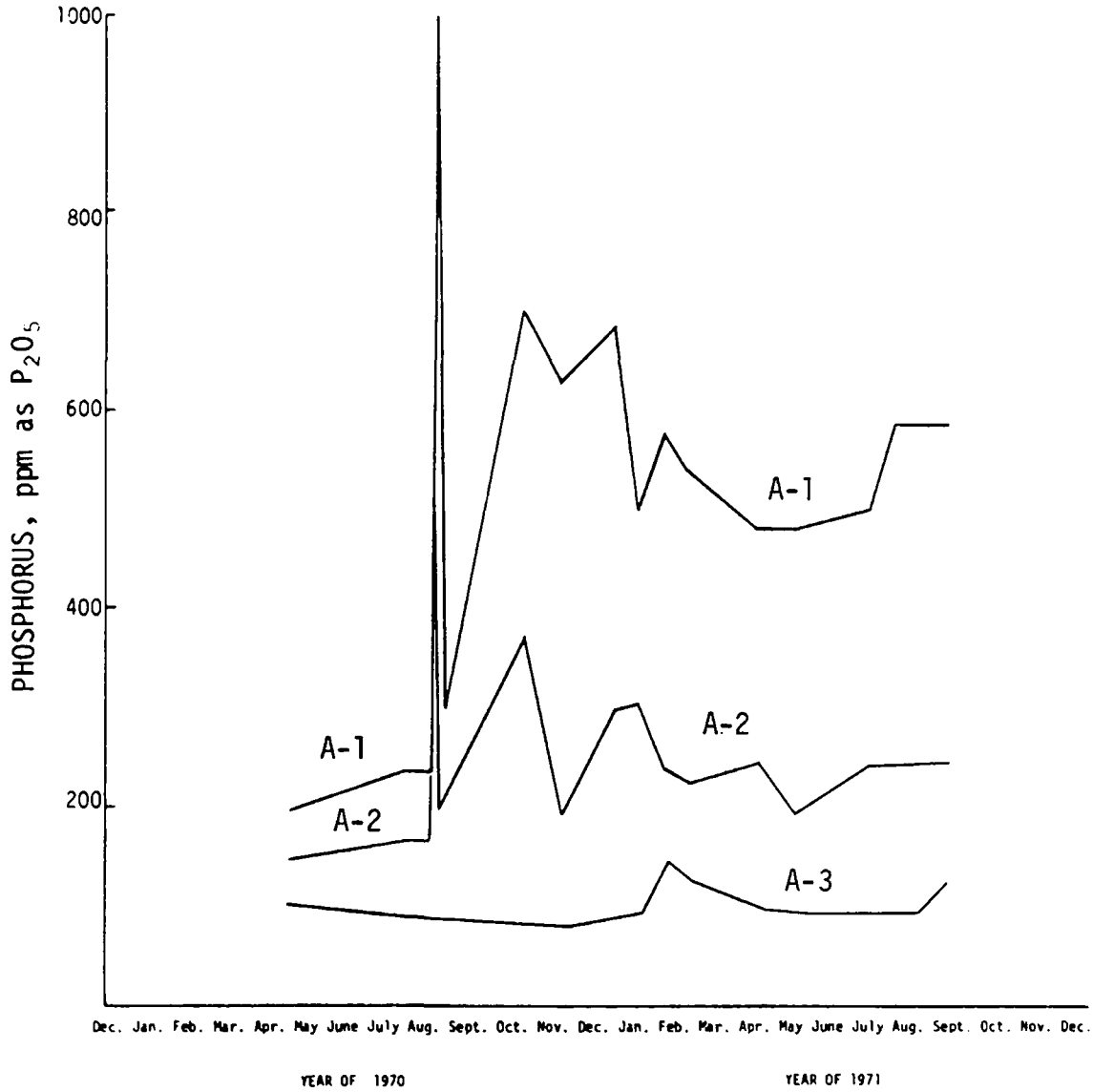
FIGURE 14




NITROGEN CONTENT OF SOIL

PLOT A-2

FIGURE 15



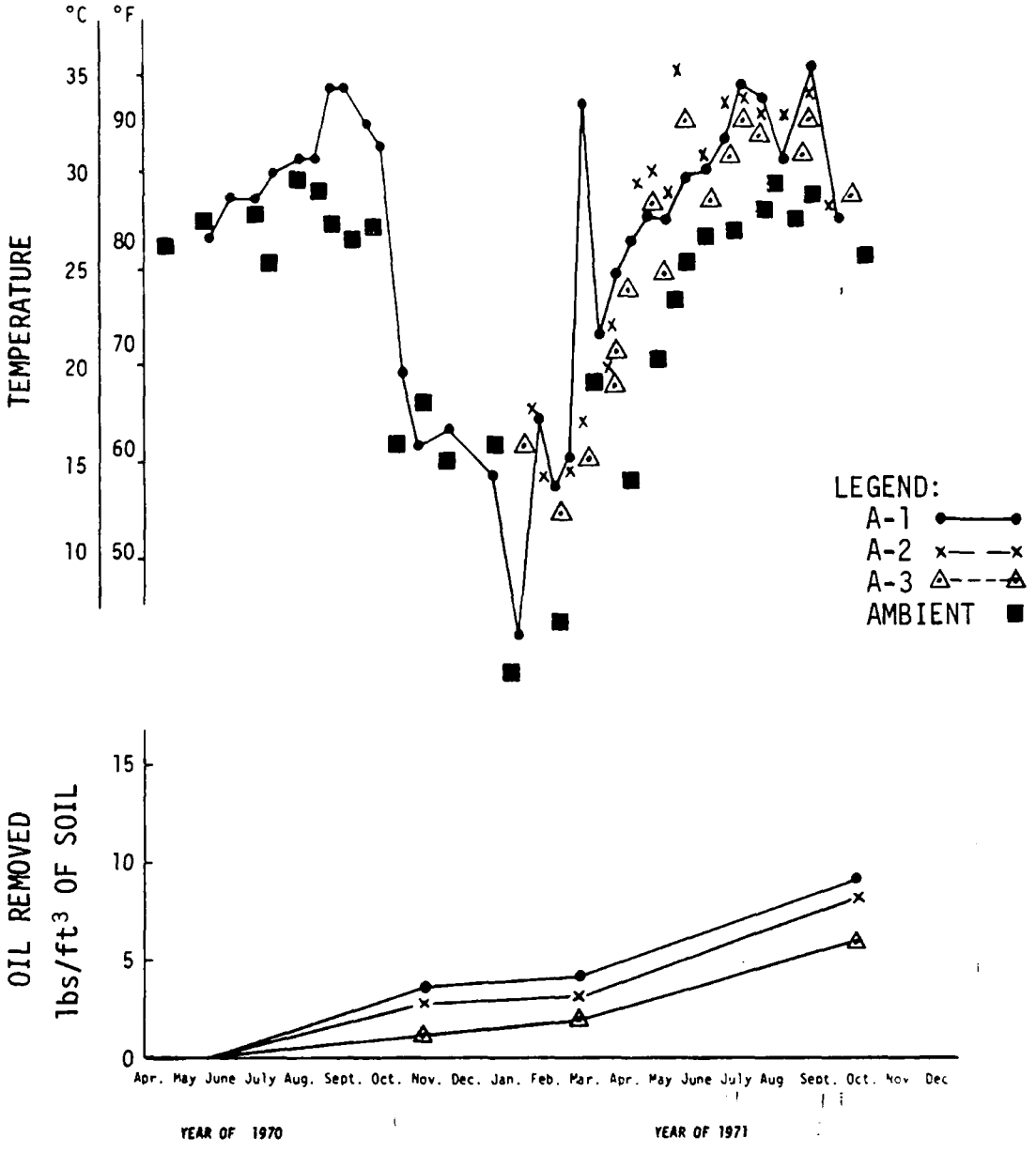

PHOSPHORUS CONTENT OF SOIL

was strong in the test plot area during cultivation periods. When this was observed, the frequency of cultivations was increased from once per two weeks to once per week or more (Appendix A, Table 5). The next addition was in January 1971, and ammonium nitrate ($NH_4NO_3$) was used instead of urea since the presence of nitrate was desirable according to our microbiology consultant. Also, a dosage of potash was recommended and added at this time to eliminate the possibility of a potassium deficiency. The use of $NH_4NO_3$ and relatively small dosages applied more frequently (about once per three months) was practiced for the remainder of the experiment. The lower concentrations of $NH_3$ for the No. 2 plot shown in Figure 14 did not emit a detectable odor, but the cultivation frequency was the same for all test plots including the unfertilized No. 3 plot. Soluble phosphorus (phosphate expressed as $P_2O_5$) contents of the soil, shown in Figure 15, did not appear to be a limiting factor. During June and July 1970, the test plots treated with bunker C (No. 6) fuel oil appeared to be repelling water. Exploratory tests indicated additional phosphorus fertilizer improved the wetting characteristic of the oily soil. Again, with the advice of a consultant, relatively large quantities (2500 ppm as $P_2O_5$ to the No. 1 plots and 600 ppm as $P_2O_5$ to the No. 2 plots) of phosphorus fertilizer were added. Differences in oil decomposition rates for the No. 1 and No. 2 plots are likely due to the fluctuating nitrogen contents rather than to the relatively constant phosphorus concentrations. The effects of fertilizer on the oil decomposition rate as related with temperature are shown in Figures 16, 17, and 18 for plots "A", "B", and "C", respectively.

The pounds of oil removed per cubic foot of soil (based upon a soil weight of 100 $lbs/ft^3$) during the project are shown to be about 15 pounds for A-1 and A-2, which had been fertilized, and about 10 pounds for the A-3 plot which was not fertilized (Figure 16). Oil removal rates for the "B" plots (Figure 17) were about 25, 20, and 12 $lbs/ft^3$ of soil for B-1, B-2, and B-3, respectively, and for the "C" plots (Figure 18) were about 25, 20, and 10 $lbs/ft^3$ for C-1, C-2, and C-3, respectively. These data indicate a direct relationship between the quantity of fertilizer added and oil removal rate. Each of these plots show the oil removal rate to be minimal during the winter months when the temperature was below about $70^oF$ ($20^oC$). However, as discussed earlier, the concentration of oil in the soil was near the starting oil content during this same period, and the apparent effect of temperature may have been coincidental.

The oil decomposition rate expressed in pounds of oil per month per cubic foot of soil are given in Table 3. The decomposition rate for the periods May to November 1970, and February to October 1971, averaged 0.90, 0.94, and 0.71 $lbs/ft^3/mo$ for A-1, A-2, and A-3; 1.79, 1.67, and 0.83 $lbs/ft^3/mo$ for B-1, B-2, and B-3; and 1.73, 1.25, and 0.67 $lbs/ft^3/mo$ for C-1, C-2, and C-3, respectively. For the three-month period of November 1970 to February 1971, the oil decomposition rate was minimum. The average decomposition rate per year at these

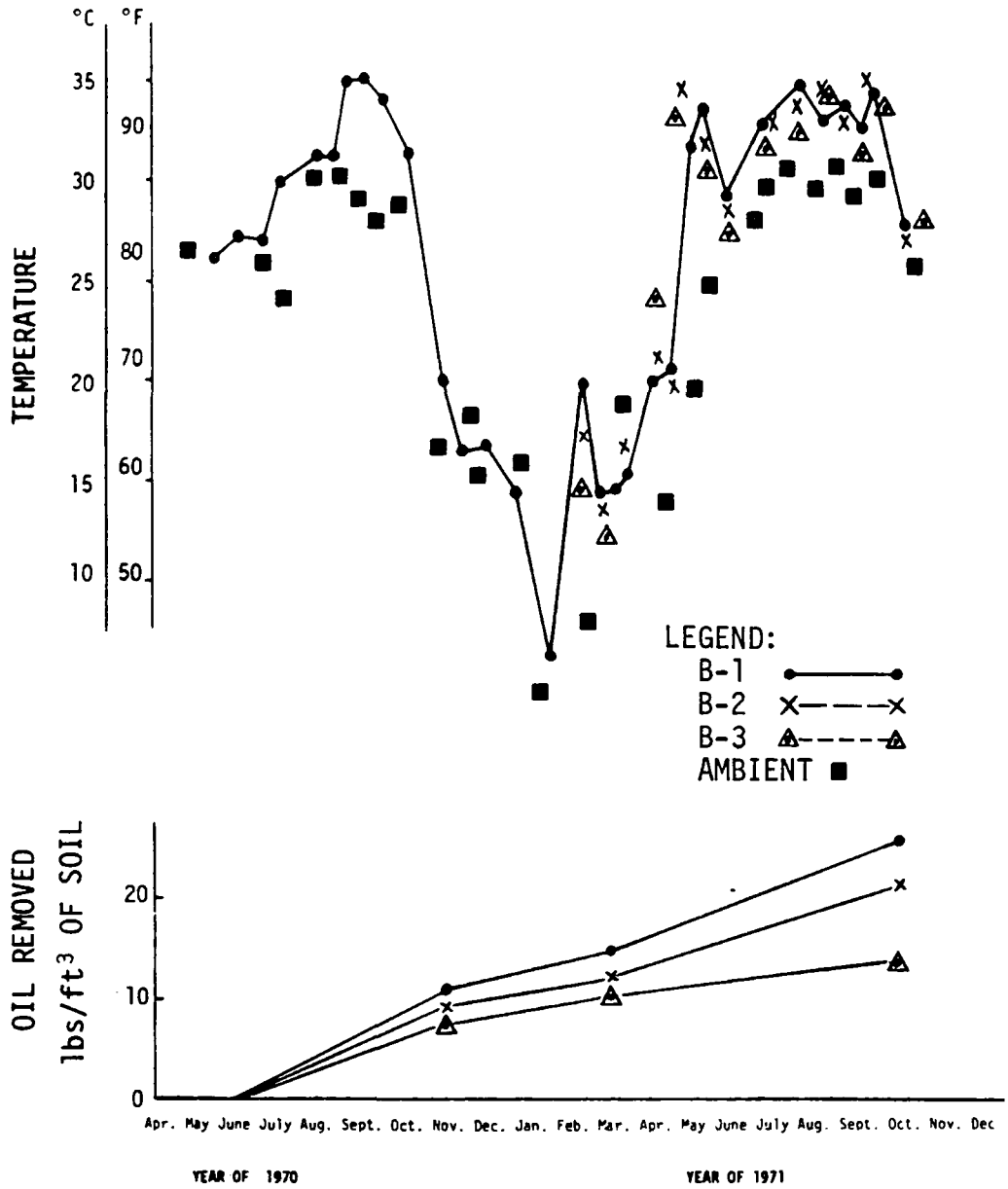
FIGURE 16




TEMPERATURE-DECOMPOSITION RATE RELATIONSHIP

"A" PLOTS

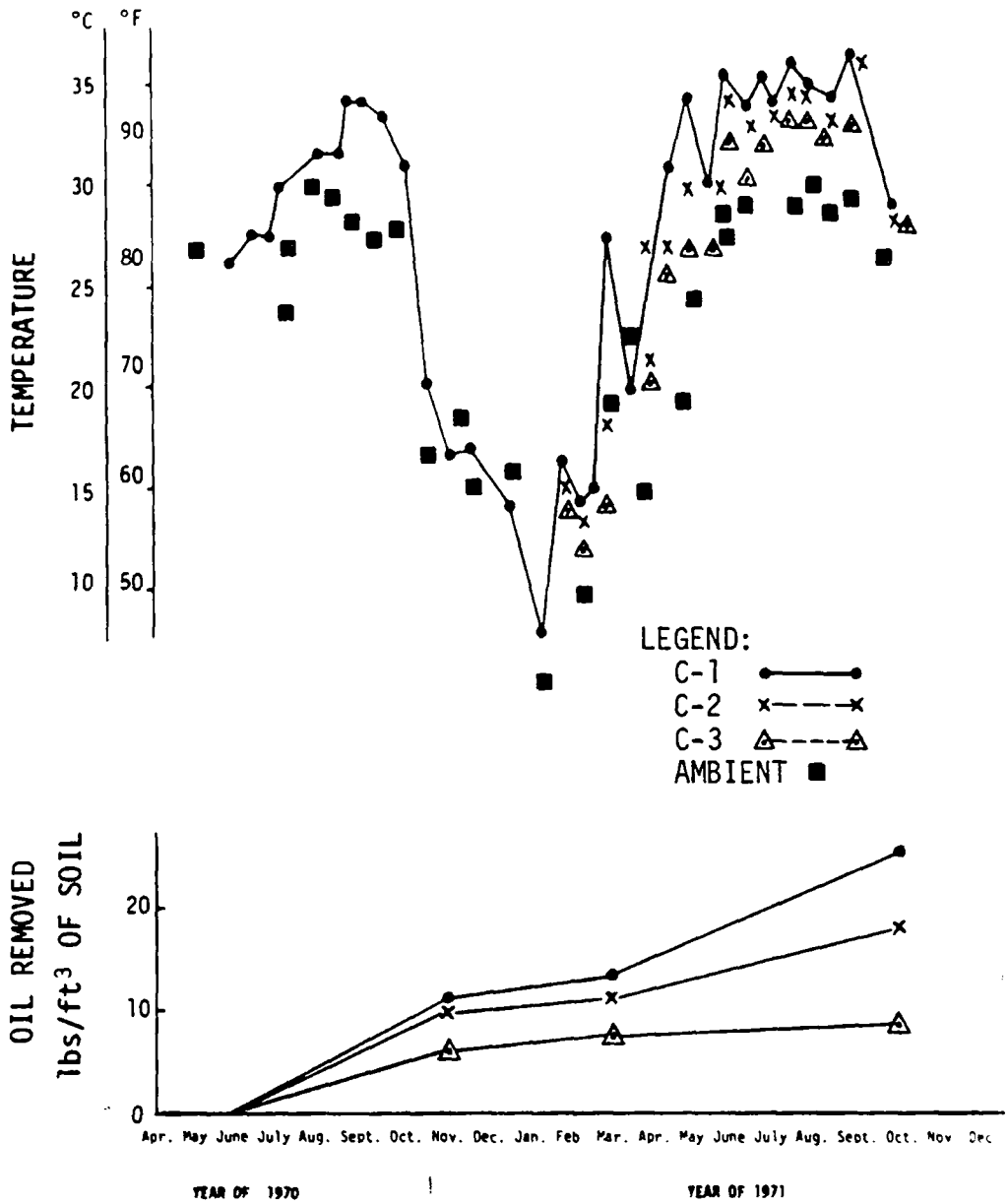
FIGURE 17




TEMPERATURE-DECOMPOSITION RATE RELATIONSHIP

"B" PLOTS

FIGURE 18




TEMPERATURE-DECOMPOSITION RATE RELATIONSHIP

"C" PLOTS

TABLE 3

OIL DECOMPOSITION RATE
POUNDS OF OIL PER MONTH PER CUBIC FOOT OF SOIL

| Plot | May to Nov. 1970 | Feb. to Oct. 1971 | Average | Nov. 1970 to Feb. 1971 | Average Per Year |
|---|---|---|---|---|---|
| A-1 | 0.67 | 1.12 | 0.90 | Minimum | 0.67 |
| A-2 | 0.50 | 1.37 | 0.94 | Minimum | 0.70 |
| A-3 | 0.17 | 1.25 | 0.71 | Minimum | 0.53 |
| B-1 | 1.83 | 1.75 | 1.79 | Minimum | 1.34 |
| B-2 | 1.83 | 1.50 | 1.67 | Minimum | 1.25 |
| B-3 | 1.16 | 0.5 | 0.83 | Minimum | 0.62 |
| C-1 | 1.83 | 1.62 | 1.73 | Minimum | 1.30 |
| C-2 | 1.50 | 1.0 | 1.25 | Minimum | 0.94 |
| C-3 | 0.83 | 0.50 | 0.67 | Minimum | 0.50 |
| 1 | | | | | 1.10 |
| 2 | | | | | 0.96 |
| 3 | | | | | 0.55 |

test conditions was 1.10, 0.96, and 0.5 lbs/ft$^3$/mo for heavily fertilized No. 1, medium fertilized No. 2, and unfertilized No. 3 plots, respectively. Therefore, fertilization with the medium quantity added to the No. 2 plots increased the oil decomposition rate about 75 percent over the unfertilized No. 3 plots, and the larger quantity of fertilizer added to the No. 1 plots increased the oil decomposition rate 100 percent. Variations in the effect of fertilizer are apparent. For the "A" plots during the period February to October 1971, the oil decomposition rate for the No. 2 and No. 3 plots exceeded the reduction for the No. 1 plot, indicating the fertilizer addition to the No. 1 plot was excessive. Also, for the "B" plots during the period May to November 1970, the oil removal rate for the No. 2 plot was the same as for the No. 1 plot, indicating the additional fertilizer applied to No. 1 plot was not needed. An optimum fertilization program would appear to be 1) addition of slightly excess quantities of phosphorus and potassium, on a one-time basis, and 2) the addition of nitrogen in the form of ammonium nitrate in small dosages as needed based upon tests to maintain a positive (10 to 50 ppm) $NH_3$ and/or $NO_3$ content.

## Metals Contents of Soils

Metals obtained with different soil extracting solvents, total nitrogen, total sulfur, and total phosphorus are given in Tables 8, 9, and 10 of Appendix A for the "A", "B", and "C" plots, respectively. The data show inconsistencies and real effects of the metal components are not apparent. Copper, zinc, and lead are normally considered to exhibit harmful effects on biological growth. These elements may have been insoluble at soil pH conditions and not available to the microorganisms.

## Oil and Nutrient Infiltration

Oil and nutrient concentrations at depths of 2, 4, and 6 feet (Table 11 of Appendix A) show these constituents did not infiltrate the soil under the conditions of the project. As discussed earlier, oil was present at the two-foot depth at the start of the study, and no change was noted after 18 months. The presence of phosphate at the two-foot depth was expected since the initial grading and leveling operations mixed the top two feet of soil.

TABLE 4

QUANTITY AND COST BASED UPON EXPERIMENTAL CONDITIONS

Calculations For Sludge Containing 100 Percent Oil:

| | QUANTITY | DOLLARS | TOTAL DOLLARS PER MONTH | DOLLARS PER BARREL |
|---|---|---|---|---|
| OIL DECOMPOSED/MONTH | | | | |
| POUNDS/CUBIC FOOT | 1 | | | |
| POUNDS/SQUARE FOOT | 0.5 | | | |
| POUNDS/ACRE | 21,780 | | | |
| GALLONS/ACRE | 2,904 | | | |
| BARRELS/ACRE | 69.14 | | | |
| SPREADING COST/ACRE | | 70.00 | 70.00 | |
| FERTILIZER | | | | |
| NITROGEN, POUNDS/YEAR | 1,000 | | | |
| COST/POUND | | 0.15 | | |
| COST/MONTH | | 12.50 | 12.50 | |
| PHOSPHORUS, POUNDS/YEAR | 500 | | | |
| COST/POUND | | 0.145 | | |
| COST/MONTH | | 6.00 | 6.00 | |
| SPREADING COST/ACRE | | 60.00 | 5.00 | |
| CULTIVATION, HOURS/PLOWING | 8 | | | |
| COST/HOUR | | 25.00 | | |
| COST/2 PLOWINGS | | | 400.00 | |
| | | | 493.50 | 7.15 |

Calculations For Sludge Containing 33 Percent Oil:

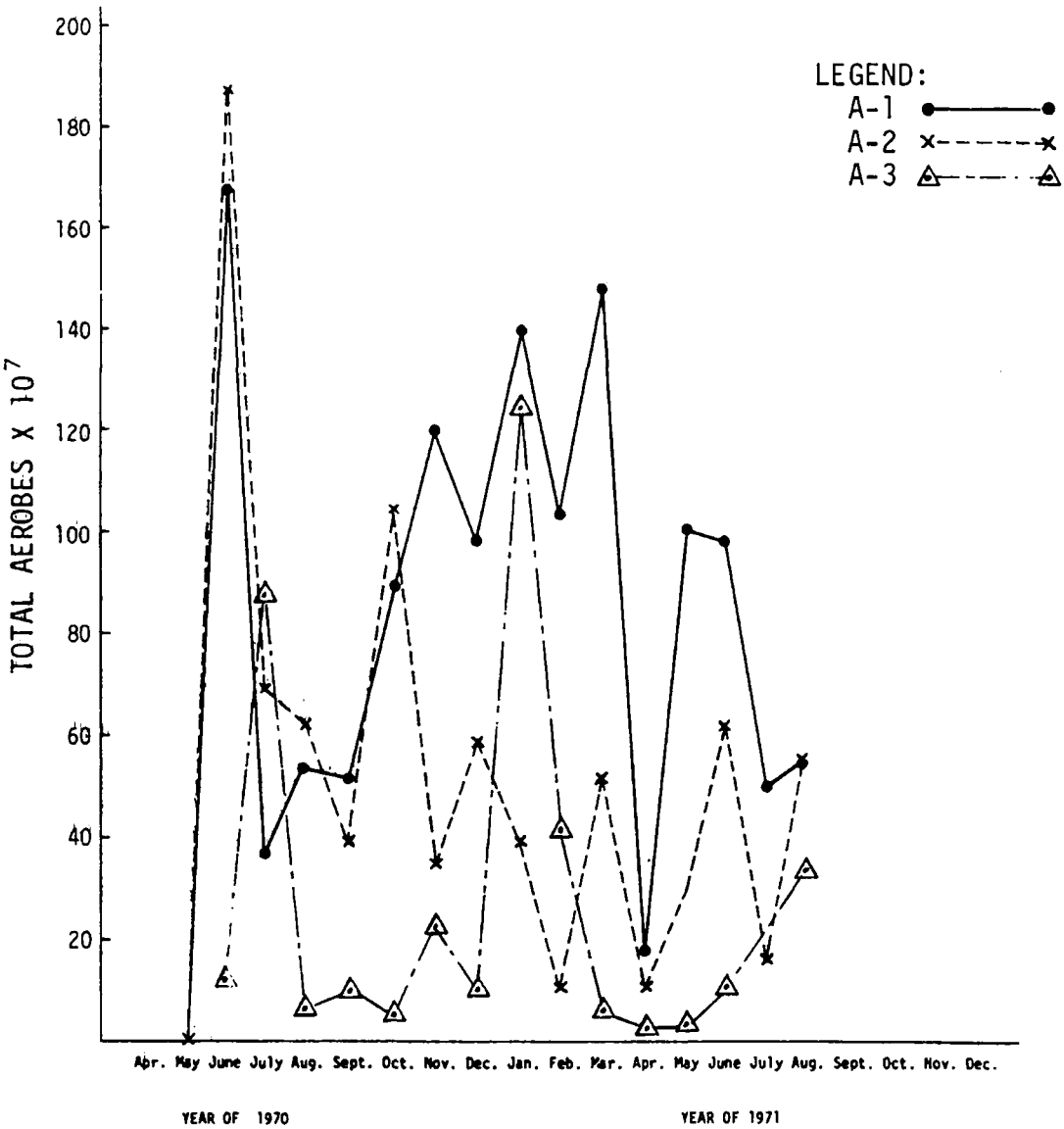
| | | | | |
|---|---|---|---|---|
| DECOMPOSED/MONTH | | | | |
| BARRELS/ACRE | 210 | | | |
| SPREADING COST/ACRE | | 210.00 | 210.00 | |
| FERTILIZER | | | | |
| MATERIAL AND SPREADING | | | | |
| (SAME AS ABOVE) | | | 23.50 | |
| CULTIVATION | | | | |
| (SAME AS ABOVE) | | | | |
| COST/2 PLOWINGS | | | 400.00 | |
| | | | 633.50 | 3.00 |

## SECTION XI

## QUANTITY AND COST BASED UPON CONDITIONS DURING THE PROJECT

The pounds of oil decomposed per cubic foot of soil per month from Table 3 were 1.10, 0.96, and 0.55 for the Nos. 1, 2, and 3 plots, respectively. A quantity of 1.0 $lb/ft^3/mo$ was selected as the basis for determining cost of the process. The fertilizer requirement was assumed to be 1,000 pounds of nitrogen and 500 pounds of phosphorus per acre per year, and costs for spreading oil and fertilizer and cultivating the soil were based upon the expense incurred during the project period. The quantities and costs based on experimental conditions are given in Table 4. An oil decomposition rate of 1 $lb/ft^3/mo$ is equal to 21,780 lbs/acre/mo or about 70 bbls/acre/mo. The cost for delivering the oil to the area and distributing the oil over the surface of the soil was about $1/bbl and for 70 bbls/acre/mo would cost $70/acre/mo. The fertilizer material and labor for spreading costs prorated on a monthly basis was estimated to be about $23.50/mo. Cultivation would require about 8 hrs/acre at $25.00/hr and two plowings/mo totals $400.00/mo. The total cost/acre/mo was estimated to be $493.50 or about $7.15 per barrel of oil. On a basis of oily sludge which may contain 33 percent oil, the total volume to be delivered and spread would be 210 barrels and would cost $210 instead of $70 for 100 percent oil. The cost for disposal of oily sludge would be about $3.00 per barrel.

FIGURE 19




MICROBIAL CONTENT OF SOIL FROM "A" PLOTS

## SECTION XII

## MICROBIAL ACTION

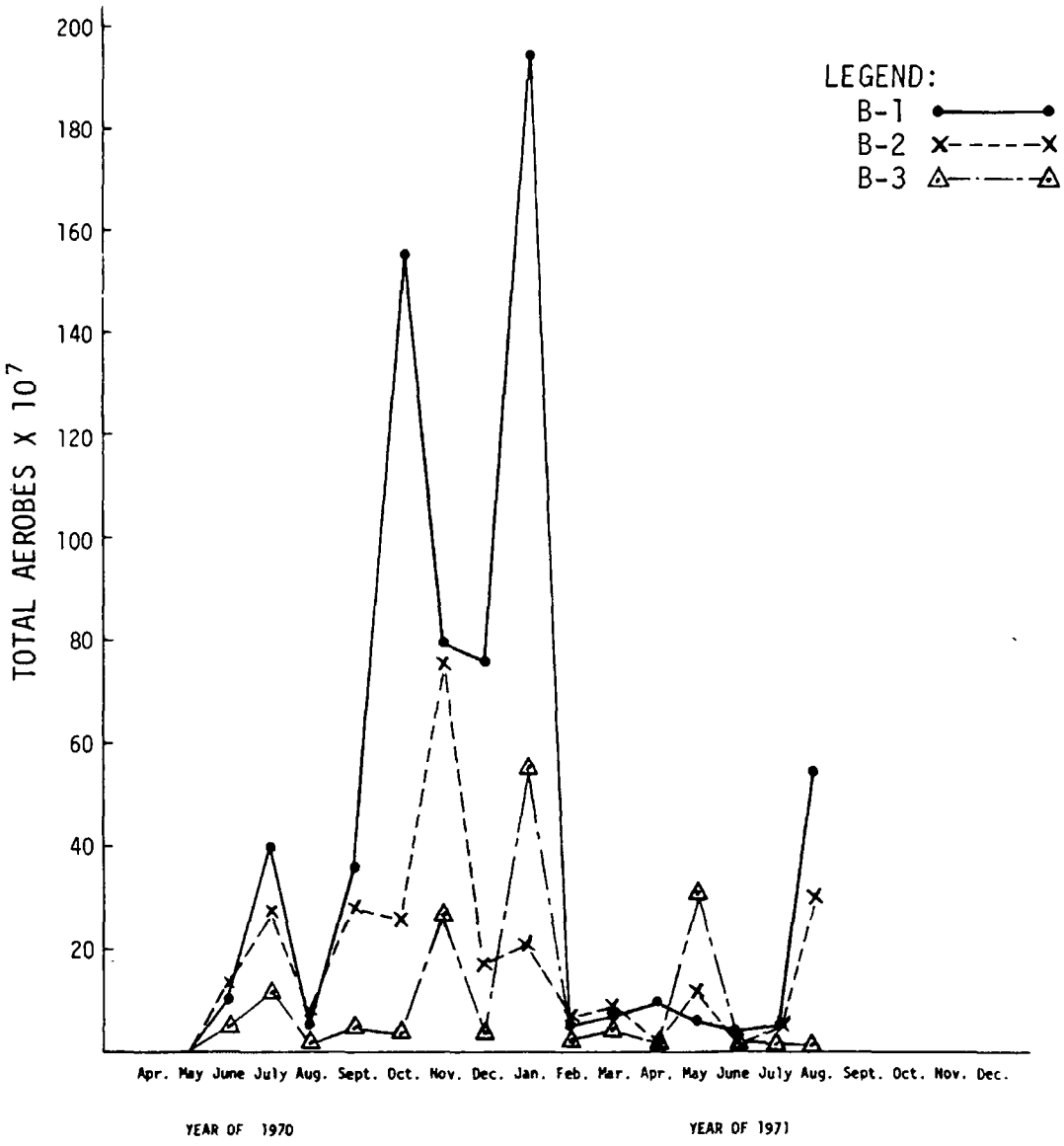
A natural function of microorganisms found abundantly in soil is to decompose nitrogenous and carbonaceous materials into microbial cellular matter. Side products of gases and partially reacted organics ("humus") are formed. When oil or hydrocarbon is the only source of carbon, oil degrading microorganisms survive and become the predominant species. An intermediate product is organic acids as discussed later.

Results of monthly determinations of the predominant organisms and a brief description from literature of individual organisms are given in Appendix B.

Due to mixing of various depths of soil in the initial grading and leveling operations, the microbial population was different on all plots. However, the microbial population contained oil decomposing bacteria especially of the Flavobacterium and Pseudomonas species. During the project period, distribution of the microorganism species was not greatly different as shown in Tables 1, 2, and 3 of Appendix B for the three oils used in the experiment. During the first eight months, the Flavobacterium, Nocardia, Pseudomonas, and Arthrobacter appeared to be most prominent in all plots. During the last nine months, Corynebacterium increased in prominence and Arthrobacter was seldom a prominent species. Also, during the latter part of the experiment, yeast was found prominent in numerous samples. The addition of fertilizer did not appear to materially affect the distribution of microorganisms but did affect the total aerobic count. The total aerobic count for "A", "B", and "C" plots are given in Tables 5, 6, and 7 of Appendix A and shown graphically in Figures 19, 20, and 21. The No. 1 plots (heavily fertilized) generally were higher in total aerobic count than No. 2 (medium fertilized) and No. 3 (not fertilized) plots. Also, the addition of oil in May 1970 and February 1971 appeared to upset the soil microbial equilibrium and caused the total aerobic count to be low.

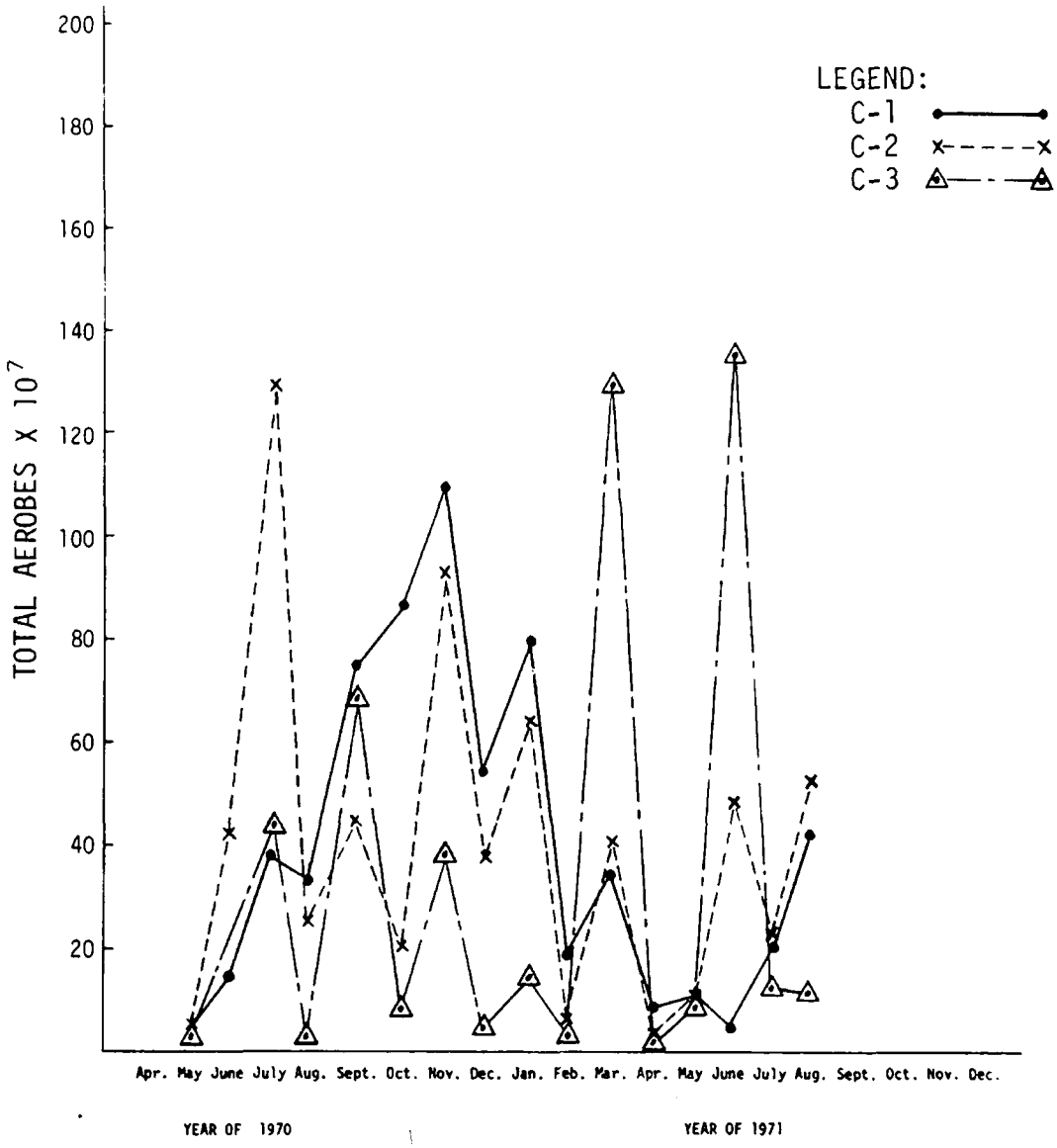
An exploratory experiment was made to determine the effect of adding oil (same as used on a specific test plot during the project period) to the nutrient agar used in the microbial analyses. The primary effect appeared to be a lower total cell count for the oil containing agar. Data from this exploratory test, plus summarized data and comments by the consultant concerning the microbial analyses of the total project period, are given in Appendix C.

FIGURE 20



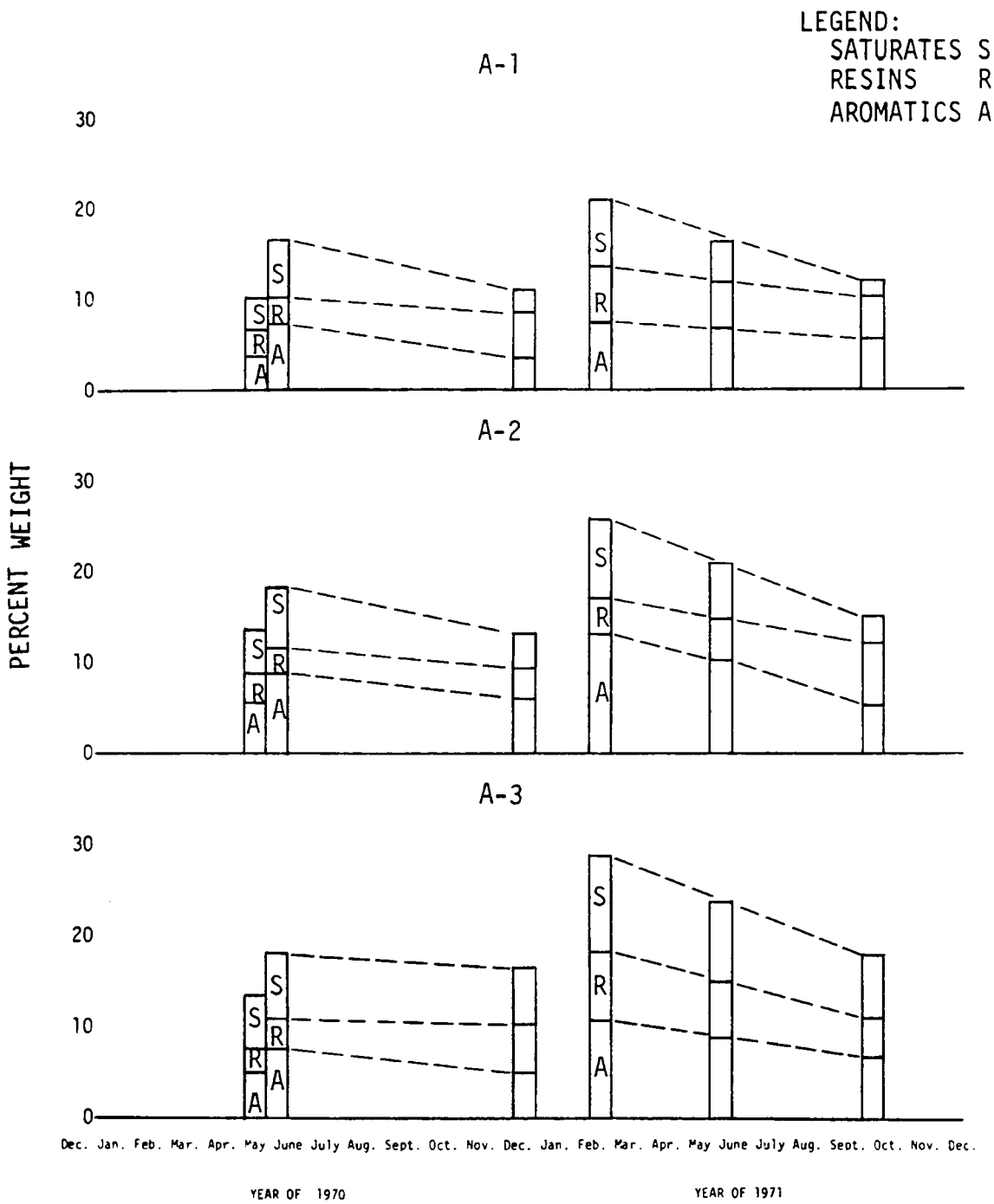

MICROBIAL CONTENT OF SOIL FROM "B" PLOTS

FIGURE 21




MICROBIAL CONTENT OF SOIL FROM "C" PLOTS

FIGURE 22




HYDROCARBON TYPE FOR "A" PLOTS

## SECTION XIII

## COMPOSITION OF OIL EXTRACTED FROM THE SOIL

Oils added to and extracted from soil plots were 1) quantitatively analyzed by a clay gel adsorption method[9] for hydrocarbon types (total saturates, resins, and aromatics); 2) qualitatively analyzed by infrared absorption for "fingerprinting" differences in oils from the various test plots; and 3) qualitatively analyzed by gas chromatography for retention times relative to normal paraffin carbon numbers. Also, the gas chromatography method[7] was used to obtain a boiling point profile (up to about 510°C) relative to percent weight of the oil.

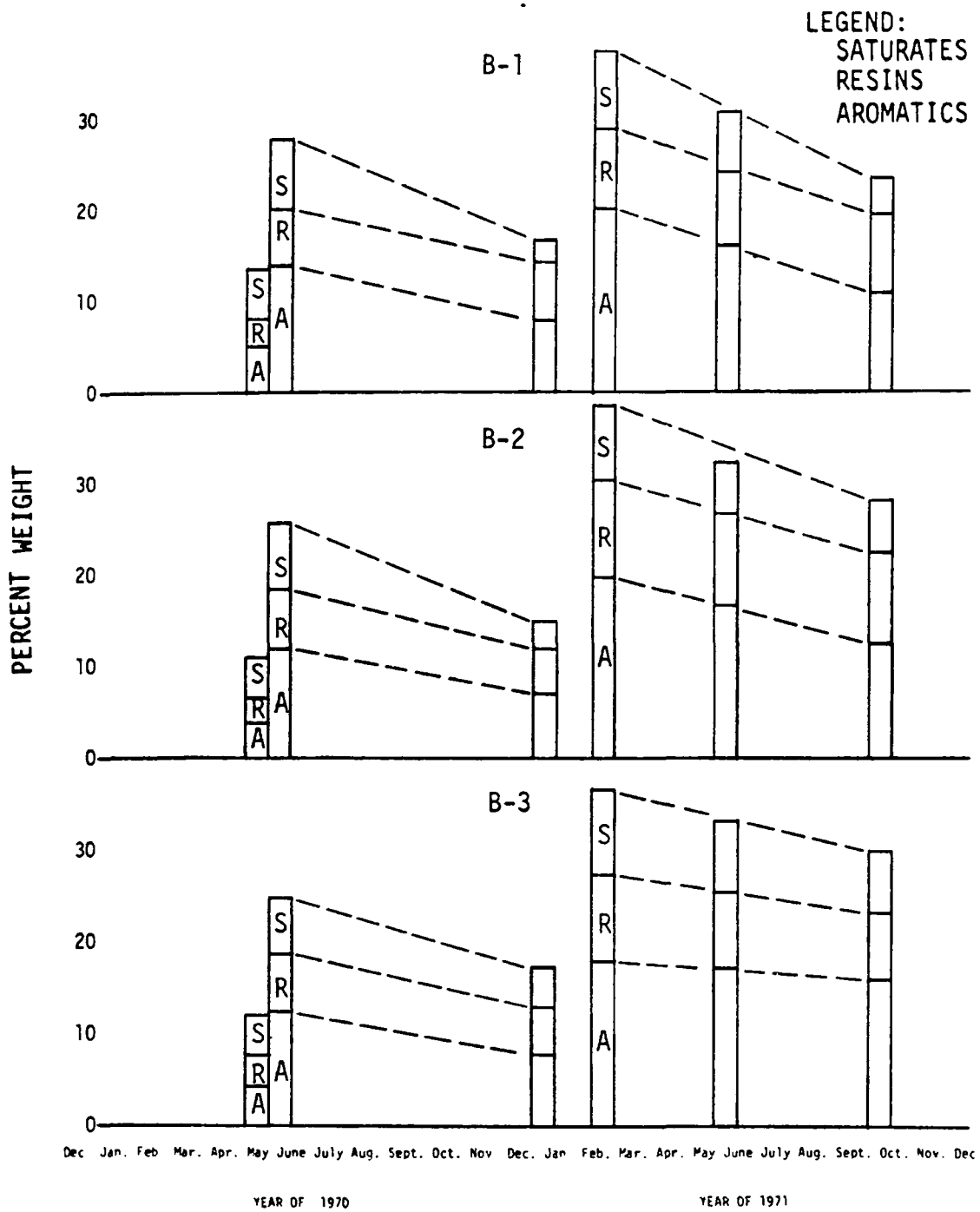
### HYDROCARBON TYPES

The clay gel method[9] utilizes clay to retain the strongly polar constituents (asphaltenes, organic acids, etc.) and designates them as resins. Silica gel is then used to separate the saturate and aromatic fractions. Hydrocarbon types from Tables 12, 13, and 14 of Appendix A are related with time and shown in Figures 22, 23, and 24 for Plots "A", "B", and "C", respectively. For the "A" plots which were treated with crude oil tank bottoms, the saturate and aromatic contents decreased and the resin content increased, indicating a conversion of saturates and/or aromatics to resinous material. The magnitude of the change appeared greatest for the No. 1 plot and least for the No. 3 plot. The change for No. 2 plot was intermediate between A-1 and A-3, indicating an effect of added fertilizer material. For the "B" plots which were treated with bunker C fuel oil, the saturate and aromatic contents decreased and the resin content appeared to remain unchanged, possibly indicating a relatively nonreactive resinous fraction. The magnitude of change for B-1 and B-2 (Figure 23) appeared to be about the same and B-3 showed the least reaction. For the "C" plots which were treated with waxy raffinate, the saturate content decreased with time, the resin content appeared to increase slightly, and the aromatic content was not markedly changed, substantiating the fact that paraffins react more easily than aromatics. The three figures (22, 23, and 24) indicate more rapid changes in composition for No. 1 and No. 2 plots which were fertilized than for the No. 3 plot. Further differences in the oils from fertilized and unfertilized plots were evident from infrared and gas chromatography examinations.

### INFRARED SPECTROSCOPY

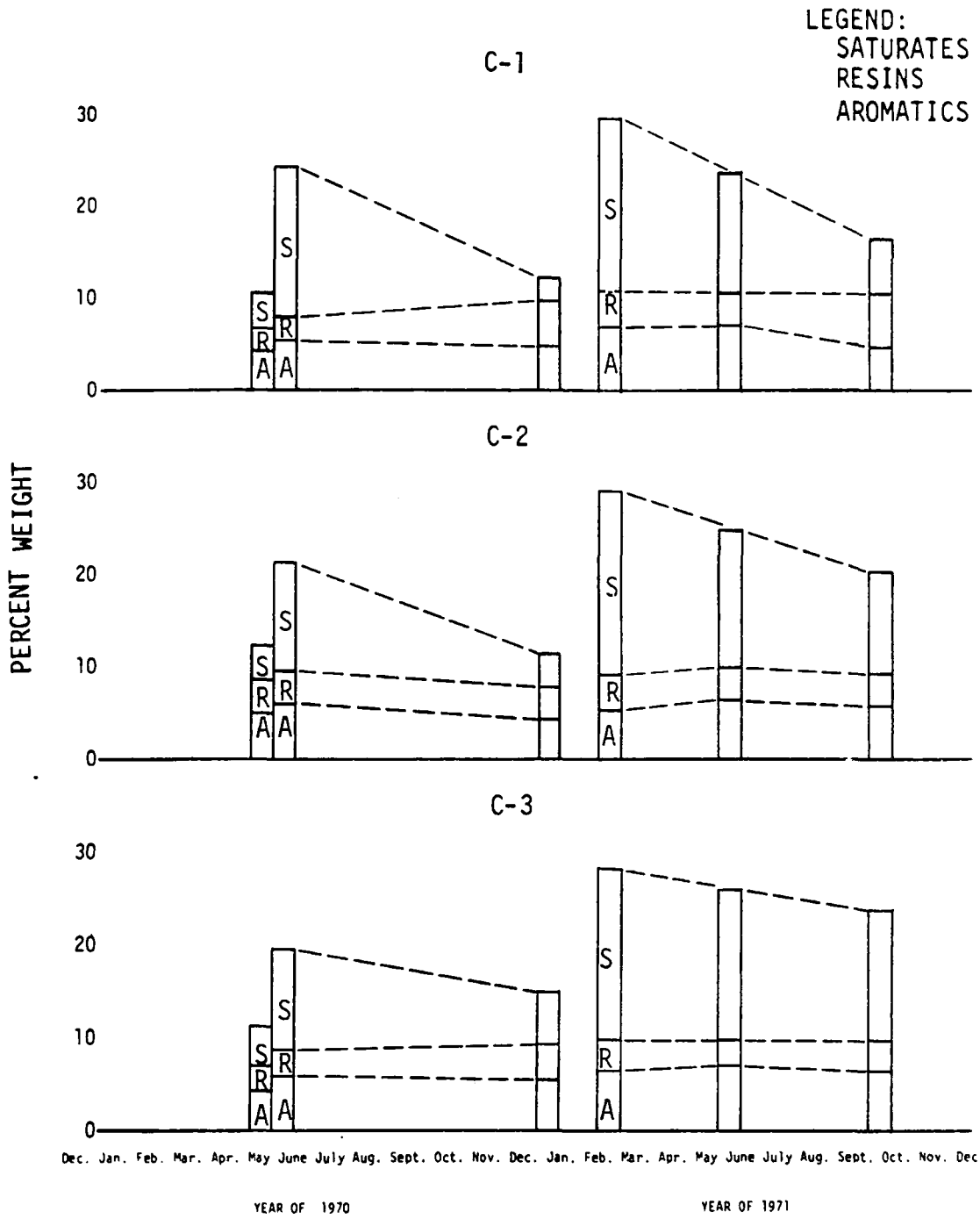
The infrared (IR) method for analyses of the oils extracted from the soil and a discussion of the analysis are given in Appendix D. The IR spectra of oil extracted from the soil after eight months and after 17 months of the project are given in Figures 25, 26, and 27 for "A", "B", and "C" plots, respectively. These figures are discussed separately in Appendix D. General conclusions from the study are as follows:

FIGURE 23




HYDROCARBON TYPE FOR "B" PLOTS

FIGURE 24




HYDROCARBON TYPE FOR "C" PLOTS

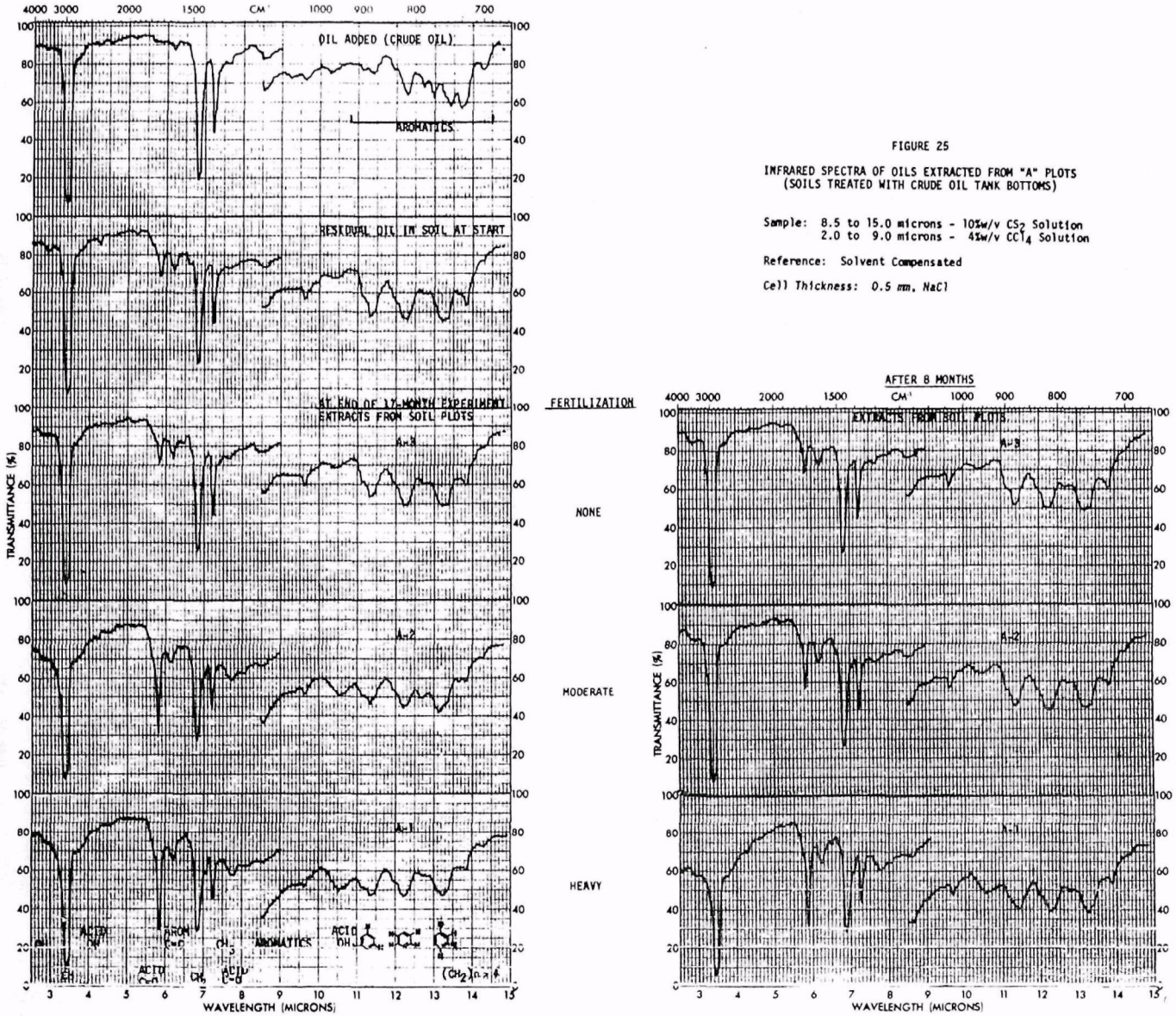



FIGURE 25

INFRARED SPECTRA OF OILS EXTRACTED FROM "A" PLOTS
(SOILS TREATED WITH CRUDE OIL TANK BOTTOMS)

Sample: 8.5 to 15.0 microns - 10%w/v $CS_2$ Solution
2.0 to 9.0 microns - 4%w/v $CCl_4$ Solution

Reference: Solvent Compensated

Cell Thickness: 0.5 mm, NaCl

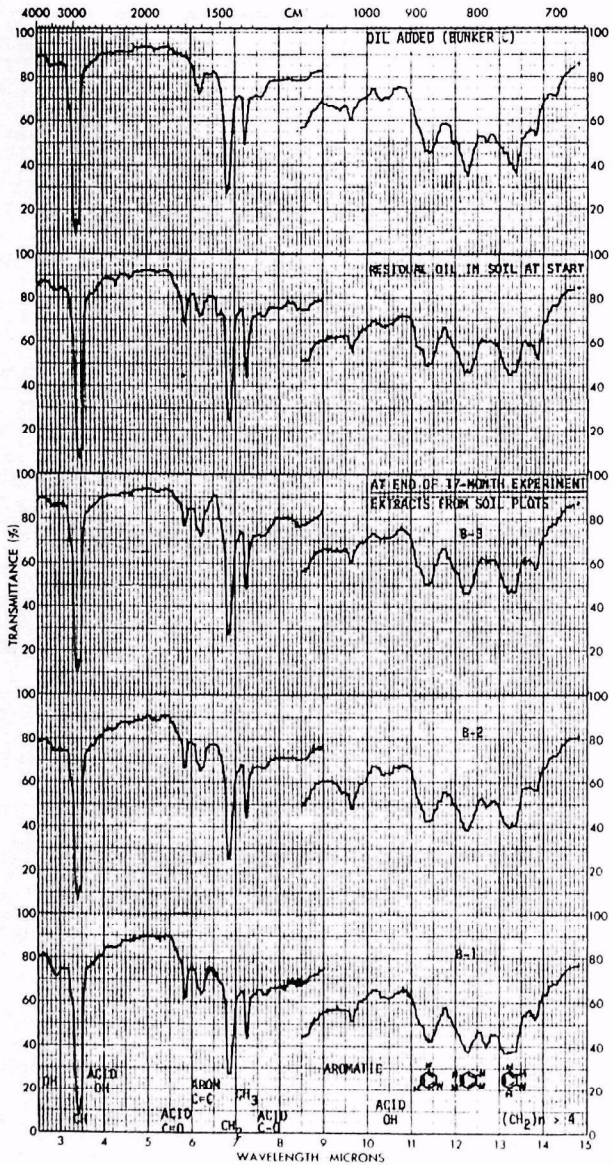


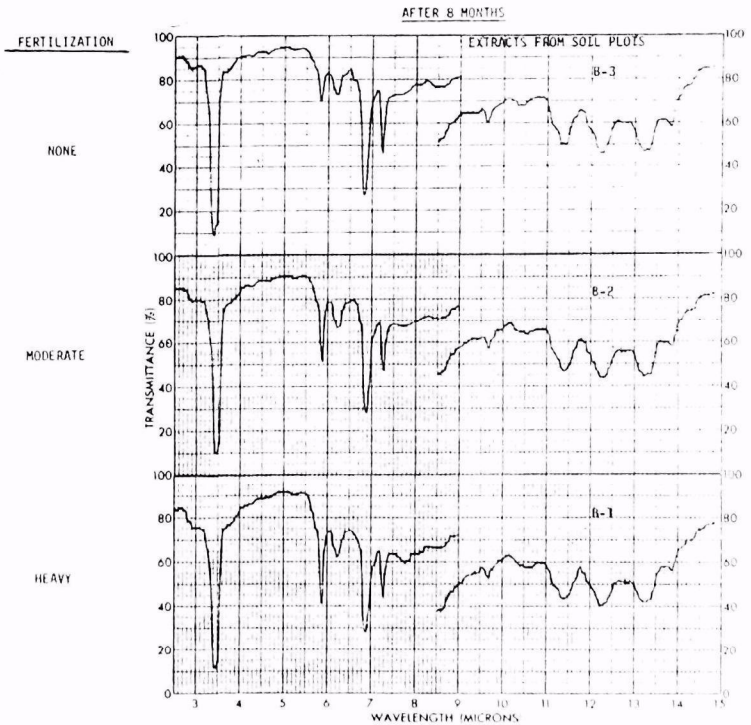

FIGURE 26

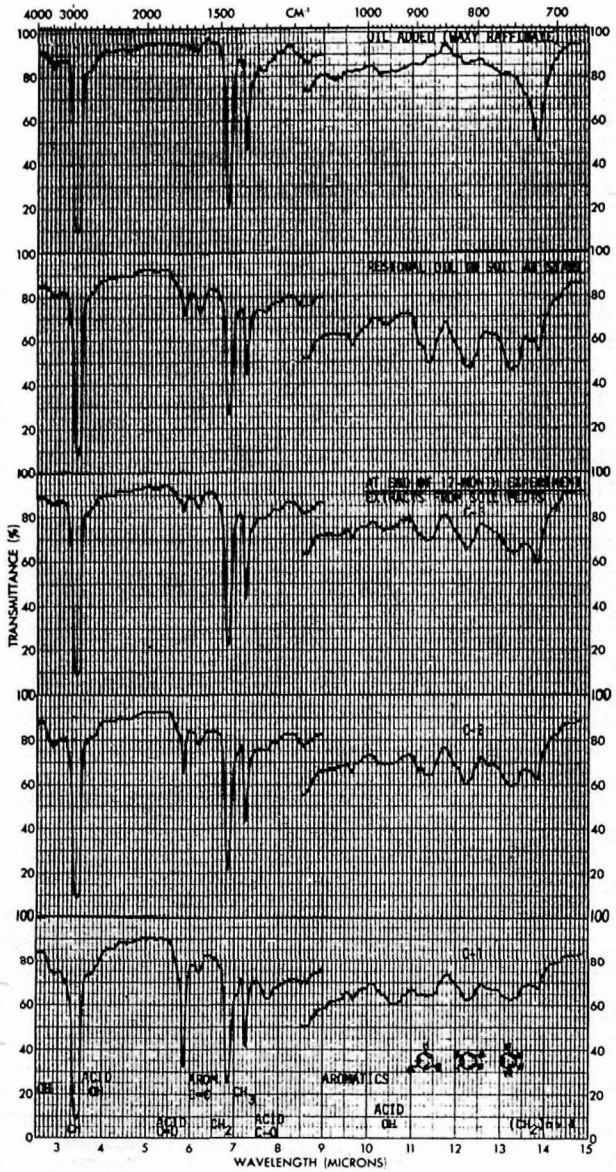
INFRARED SPECTRA OF OILS EXTRACTED FROM "B" PLOTS
(SOILS TREATED WITH BUNKER C FUEL OIL)

Sample: 8.5 to 15.0 microns - 10%w/v $CS_2$ Solution
2.0 to 9.0 microns - 4%w/v $CCl_4$ Solution

Reference: Solvent Compensated

Cell Thickness: 0.5 mm, NaCl






FERTILIZATION

NONE

MODERATE

HEAVY

AFTER 8 MONTHS

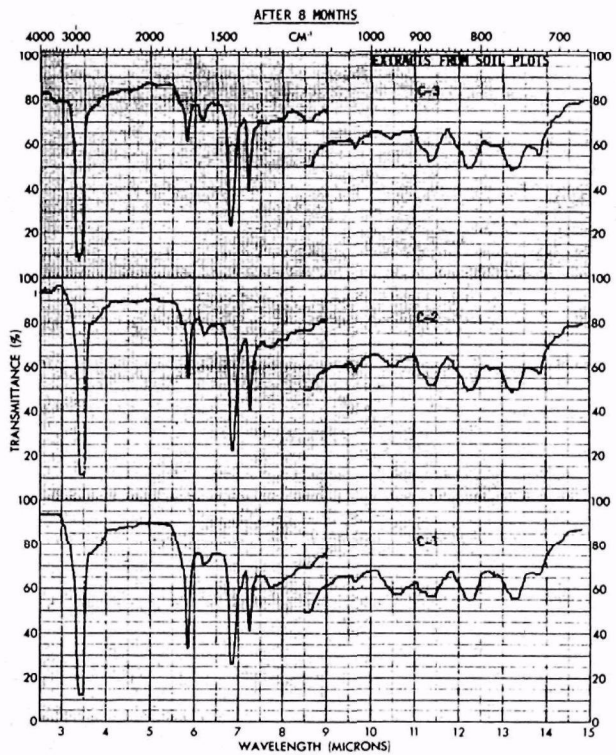



FIGURE 27

INFRARED SPECTRA OF OILS EXTRACTED FROM "C" PLOTS
(SOILS TREATED WITH WAXY RAFFINATE)

Sample: 8.5 to 15.0 microns - 10%w/v $CS_2$ Solution
2.0 to 9.0 microns - 4%w/v $CCl_4$ Solution

Reference: Solvent Compensated

Cell Thickness: 0.5 mm, NaCl

The IR spectral character of all the oils extracted from the soil plots are similar to that of the oil found in the soil at the beginning of the study, despite a substantial variation in the type of oils added to the soil. The extracted materials would be grossly characterized from the IR spectra as highly aromatic oils containing a substantial amount of condensed multi-ring aromatic structures. Organic acids were present in each of the extracted oil samples, but in varying amounts, based upon the presence of an acid carbonyl (C=O) group (absorbing at 5.85μ). The oils from plots that were fertilized show higher concentrations of organic acids, and the concentration appeared to be the greatest in the heavily fertilized plots. The increase in organic acids correlates, in general, with a decrease in the long chain paraffin (absorption at 13.88μ) and a decrease in total saturate groups (absorption at 6.86μ and 7.25μ). A substantial reduction of long chain paraffin groups was observed even in the absence of fertilizer suggesting that such groups are the most readily decomposed under the conditions existing in these studies.

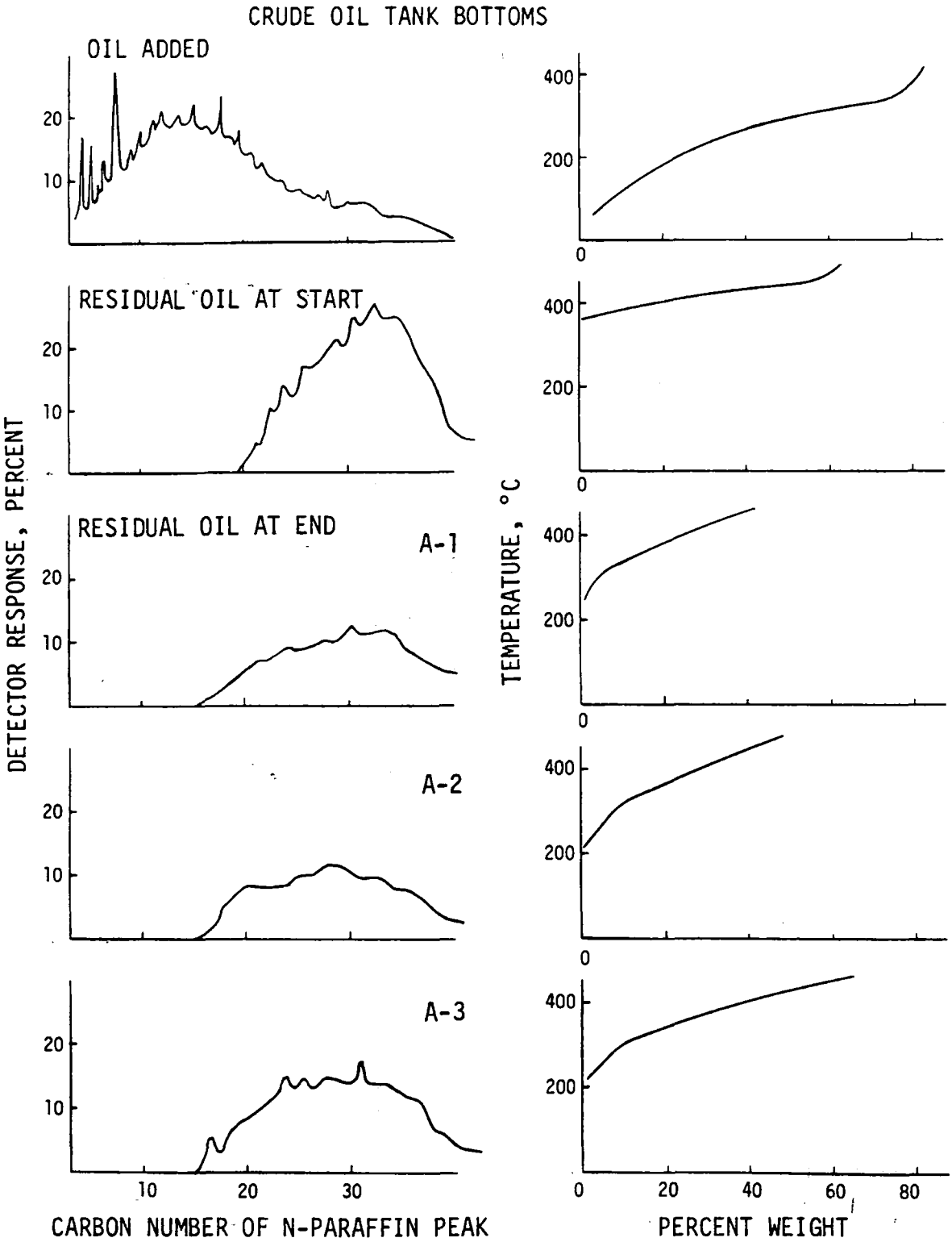
## GAS CHROMATOGRAPHY

Gas chromatographs[7] were obtained with nonpolar media which presumably makes no separation according to molecular type and permits passage of all hydrocarbon components on the basis of their boiling points. The retention times and boiling points of normal paraffins were used as a basis for determining temperatures. The detector response of a sample being analyzed indicates the quantity of hydrocarbon in the sample relative to the carbon number of normal paraffins. The gas chromatographs and boiling point profiles for the "A", "B", and "C" plots are shown in Figures 28, 29, and 30, respectively. Crude oil tank bottoms (Figure 28) contains components whose carbon numbers, relative to normal paraffins, range from about 5 to 40. The normal paraffin content was substantial, based upon a peak for each normal paraffin carbon number. The initial boiling point was less than 50°C, and about 80 percent weight of the sample boiled at a temperature less than 400°C or equivalent to about 25 carbon numbers (based upon n-paraffins). For the highest temperature reached, 511°C (equivalent to 38 n-paraffin carbon numbers), about 95 percent weight of the sample had passed through the gas chromatograph column. (Residuals were back-flushed from the column to obtain a material balance.)

Residual oil at the start of the project contained carbon numbers ranging from about 20 to >38 relative to normal paraffins. The boiling point profile ranged from about 350 to 510°C at about 70 percent weight of the sample passing through the column. Detector response peaks did not coincide with normal paraffin carbon numbers.

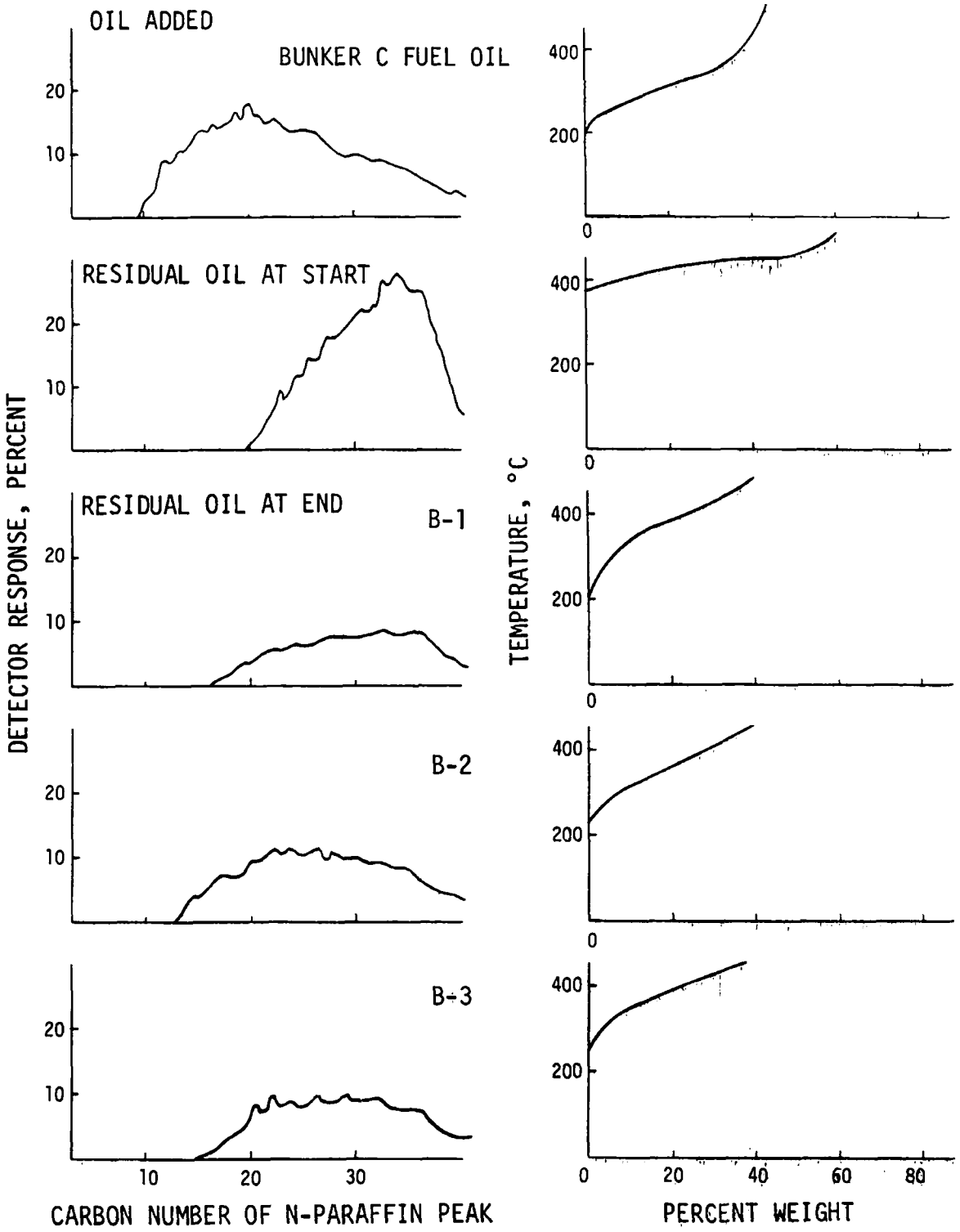
Residual oil extracted from soil plots A-1 and A-3 at the end of the project period (Figure 28) appears quite different from the oil added and the starting residual oil. The carbon number range was about 15 to >38 for each of the three oils. The initial boiling point was

FIGURE 28



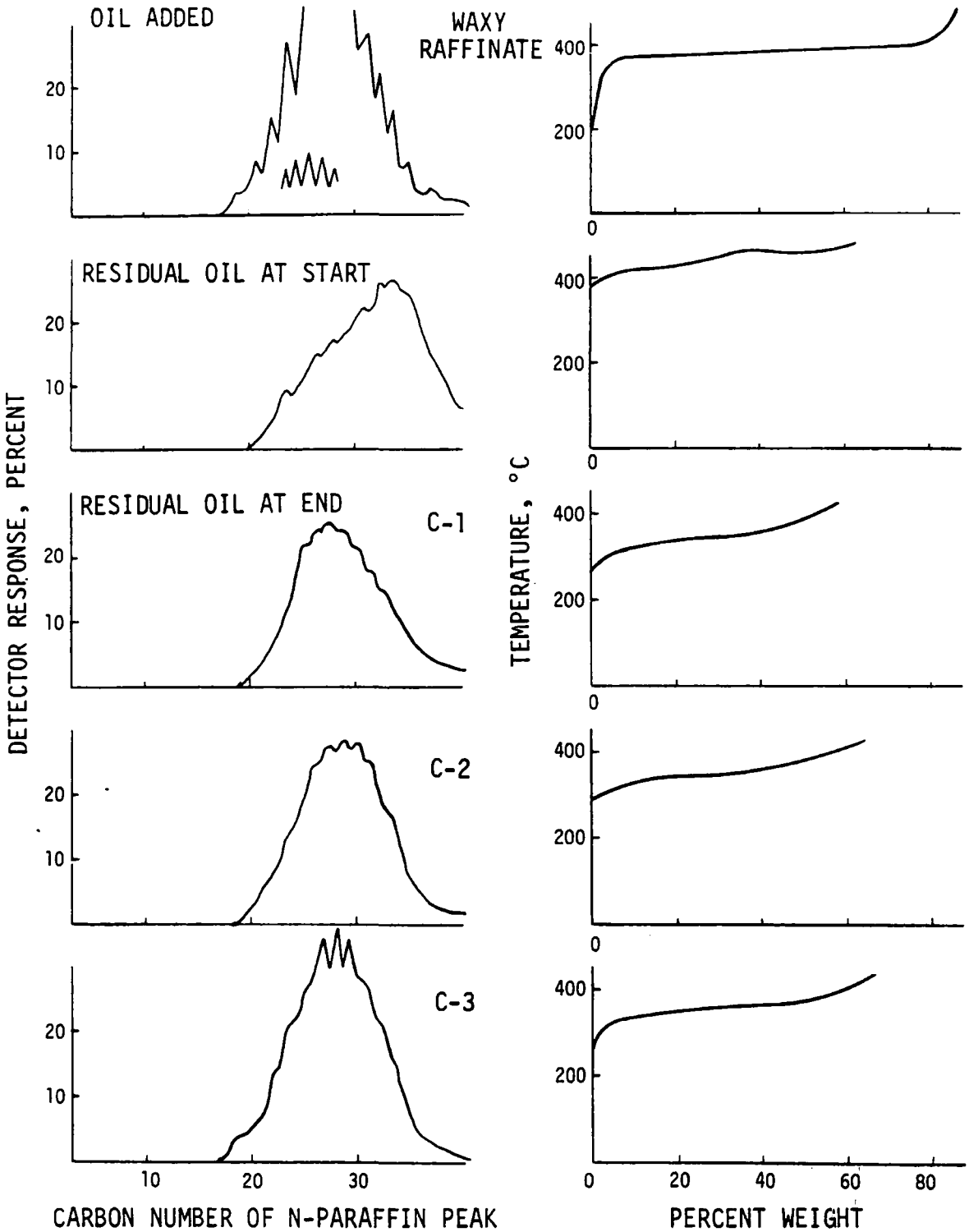

GAS CHROMATOGRAPH AND BOILING POINT PROFILES, "A" PLOTS

FIGURE 29




GAS CHROMATOGRAPH AND BOILING POINT PROFILES, "B" PLOTS

FIGURE 30




GAS CHROMATOGRAPH AND BOILING POINT PROFILES, "C" PLOTS

about 200°C and the percent weight up to 510°C was about 45 and 65 for plots A-1 and A-3, respectively. Normal paraffin peaks were not apparent for plot A-1. The detector response for oil extracted from the A-3 plot showed small peaks at carbon numbers 16, 22, 23, 25, and 28, indicating incomplete microbial reaction. Also, the residual oil at the end of the project was different from the residual oil at the start, indicating the starting residual oil had been changed during the project. Therefore, the starting residual oil was not a stable, nonreactive material.

Chromatographs and boiling point profiles for the "B" plots (Figure 29) are similar to the "A" plots discussed above. Differences appear in the percent weight boiling less than 510°C due to the higher boiling bunker C fuel oil which was added to the "B" plots. Also as expected, normal paraffin peaks for bunker C fuel oil were not apparent. Again the residual oils at the start and end of the project were different.

Results for the "C" plots which received waxy raffinate (Figure 30) show predominant normal paraffin peaks in the oil added to the soil and some definite peaks in the residual oil at the end of the project. This was expected since the hydrocarbon type analyses (Figure 24) showed unreacted saturates present for all plots (C-1 and C-3). The residual oil at the start and end (Figure 30) of the project appear different, indicating a reaction of the starting residual oil has occurred especially in the carbon number range of 30 to 35.

## SECTION XIV

## RAINFALL RUNOFF

Rainfall accumulated and was trapped in the plot area as discussed previously. Drainage of the plots was controlled, and a sample of the runoff water was obtained for analysis. On a few occasions during excess rainfall periods, water overflowed the plots. Analyses of the water for oil, ammonia, nitrate, and phosphate contents indicated that little, if any, of these constituents were present when drained immediately after a rain. Long standing appeared to cause higher oil contents. The oil content ranged from about 30 to 100 mg/l, and the oil content of water from the fertilized plots as discussed earlier were found to contain the highest concentration of organic acids. Each plot was drained about 36 times during the 18-month project, and many times the plots were only partially full but needed to be dry for cultivation. Based upon an average oil content of 60 mg/l, about 0.6 pounds of oil was discharged during the 17-month experimental period. This quantity equals about 0.03 $lbs/ft^3$ of oil in the soil, and adjustments in earlier decomposition rate determinations for such a small quantity were not considered justifiable.

Infrared examination of oil recovered from rainfall runoff water is discussed in Appendix D and indicated the oil to be organic acids with characteristics quite similar with spectra for naphthenic acids.

Ammonia content of the water appeared to vary with the soil nutrient content. During periods when the ammonia was excessive on the No. 1 plots, discharge water contained up to 150 mg/l ammonia as N. Nitrates and phosphates were generally absent in the discharges.

# SECTION XV

## ACKNOWLEDGMENTS

Facilities, personnel, and partial (30%) financial support were furnished by Shell Oil Company. A financial grant (70%) and guidance were supplied by the Environmental Protection Agency.

Dr. Melvin L. Renquist, now retired, and Dr. Ben S. Baldwin, Chief Technologist, served as Grant Directors and provided the necessary administrative assistance for the project.

Mr. C. Buford Kincannon, Senior Engineer, directed the project activities and prepared the initial and final reports.

Mr. Wilbert L. Pegues, Laboratory Technician, performed laboratory tests, supervised the experimental tasks of the plot area, and collected data.

Mr. James M. Martin, Senior Research Chemist, provided infrared spectra data and interpretation of the infrared results.

Consultants during the project were Dr. Edwin O. Bennett, Microbiologist, University of Houston, and Dr. Warren D. Anderson, Soil Specialist, Texas A&M University.

From the Environmental Protection Agency, valuable guidance was provided by Mr. Leon H. Myers, Project Officer, and the final report was reviewed by Dr. Thomas E. Short, Chemical Engineer.

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SECTION XVII

APPENDICES


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# APPENDIX A

## ANALYTICAL RESULTS

The three simultaneous experiments using crude oil tank bottoms on the "A" soil test plots, bunker C (No. 6) fuel oil on the "B" plots, and waxy raffinate on the "C" plots were similar. Properties of the oils added to the soils are given in Table 1. Oil contents of subsamples from each soil plot described in Section IX are given in Tables 2, 3, and 4 for the "A", "B", and "C" plots, respectively. Subsample results from each plot were averaged, and the averaged values are also given in Tables 5, 6, and 7. These tables also include soil moisture, pH, oil, soluble nitrogen (ammonia, $NH_3$ and nitrate, $NO_3$), soluble phosphorus (phosphate, $PO_4$, expressed as $P_2O_5$) and total aerobic microorganism content and temperature, all listed chronologically. The number of plowings between sampling dates and the oil and fertilizer addition dates have been included with the chronologically recorded data (Tables 5, 6, and 7).

Metals, nitrogen, phosphorus, and sulfur contents of the soil are given in Tables 8, 9, and 10 for test plots "A", "B", and "C", respectively. Oil and nutrient contents of soil taken at depths of 2, 4, and 6 feet are given in Table 11.

Oil extracted from the soil test plots and oil added to the soil were analyzed for hydrocarbon types, infrared and gas chromatography characteristics. Hydrocarbon types for the "A", "B", and "C" plots are given in Tables 12, 13, and 14, respectively. The infrared and gas chromatographic data are presented graphically and discussed in Section XIII. (Details of the infrared study are given in Appendix D.)

APPENDIX A

TABLE 1

OIL PROPERTIES

SIMULATED SLUDGES A, B, AND C

| | | SLUDGE | | |
|---|---|---|---|---|
| | TANK BOTTOMS | A CRUDE OIL | B BUNKER C | C WAXY PRODUCT |
| SPEC. GRAV., 60/60°F | | 0.86 | 1.03 | 0.85 |
| LBS/GAL | | 7.12 | 8.57 | 7.08 |
| POUR POINT, °F | | -5 | 40 | 95 |
| VISCOSITY, SU, 60°F | | 60 | 19,000 | - |
| SSF, 122°F | | | 120 | 59 |
| HYDROCARBON TYPE, %w | | | | |
| SATURATE | | 36 | 18 | 90 |
| RESINS | | 8 | 26 | - |
| AROMATIC | | 56 | 56 | 10 |
| TOTAL SULFUR, %w | | 0.47 | 1.96 | 0.04 |
| TOTAL NITROGEN, %w | | 0.09 | 0.41 | <0.0005 |
| TOTAL PHOSPHORUS, PPM | | 6 | 11 | 5 |
| TOTAL ASH, PPM | 31,000 | | 320 | 8 |
| CALCIUM | 1,880 | | 10 | Nil |
| MAGNESIUM | 375 | | 1 | Nil |
| SODIUM | 3,135 | | 15 | Nil |
| IRON | 1,255 | | 20 | Nil |
| COPPER | 94 | | 1 | Nil |
| LEAD | Nil | | Nil | - |

APPENDIX A

TABLE 2

OIL CONTENT OF INDIVIDUAL SOIL SAMPLES FOR "A" PLOTS
PERCENT WEIGHT

| Plot | A-1 | | | | A-2 | | | | A-3 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sub-Sample | a | b | c | avg. | a | b | c | avg. | a | b | c | avg. |
| Date | | | | | | | | | | | | |
| 4-22-70 | 8.9 | 10.8<br>10.2 | 9.6 | 10 | 11.5 | 10.6 | 10.6 | 11 | 11.1 | 10.6 | 11.0 | 11 |
| 5-13 | 8.3 | 12.1 | 9.4 | 10 | 12.7 | 12.4<br>13.6 | 14.2 | 13 | 13.6 | 13.7 | 12.1 | 13 |
| 5-19 | 13.1 | 14.7 | 12.5 | 13 | 15.0 | 16.8 | 17.2 | 16 | 14.1 | 15.2<br>14.9 | 14.4 | 15 |
| 5-27 | 11.5 | 16.1<br>15.7 | 15.4 | 14 | 15.8 | 17.6 | 14.9 | 16 | 15.4 | 16.0 | 16.0 | 16 |
| 6-11 | 13.3 | 14.9 | 14.3 | 14 | 16.4 | 18.1 | 17.3 | 17 | 15.3<br>15.5 | 17.5 | 17.2 | 17 |
| 6-24 | 14.0 | 15.6 | 15.4 | 15 | 15.5 | 16.9 | 17.6 | 17 | -- | 17.5 | 15.8 | 17 |
| 7-10 | 14.4 | 17.7 | 15.3 | 16 | 17.4 | 17.7 | 16.7 | 17 | 18.2<br>17.0 | 17.2 | 18.8 | 18 |
| 7-29 | 13.8 | 15.1 | 14.2 | 14 | 15.7 | 16.7<br>15.6 | 15.4 | 16 | 16.3 | 17.9 | 17.8 | 17 |
| 8-14 | 13.1 | 15.0 | 13.9 | 14 | 14.3 | 16.2 | 16.1 | 16 | 17.2 | 17.3<br>17.3 | 17.1 | 17 |
| 8-27 | 11.4 | 14.2 | 13.9 | 13 | 14.2 | 15.5 | 15.7 | 15 | 17.9 | 17.2<br>17.2 | 16.7 | 17 |
| 9-10 | 11.1 | 11.1 | 11.0 | 11 | 13.6 | 13.9 | 13.6 | 14 | 17.4 | 18.0<br>18.1 | 17.9 | 18 |
| 9-22 | 11.9 | 11.8 | -- | 12 | 13.6 | 13.4 | -- | 14 | 15.9 | 16.0 | -- | 16 |
| 10-16 | 11.3 | 11.3 | 11.4 | 11 | 13.4 | 13.7 | 13.4 | 14 | 16.3 | 16.0<br>16.3 | 15.5 | 16 |

APPENDIX A

TABLE 2 (CONTD.)

| Plot | A-1 | | | | A-2 | | | | A-3 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sub-Sample | a | b | c | avg. | a | b | c | avg. | a | b | c | avg. |
| Date | | | | | | | | | | | | |
| 10-30-70 | 10.1 | 11.3 | 10.3 | 11 | 12.7 | 12.9 | 13.6 | 13 | 15.4 | 16.4<br>16.2 | 15.4 | 16 |
| 11-13 | 11.4 | 12.0 | 11.0 | 12 | 12.8 | 13.8 | 14.2 | 14 | 15.4 | 16.7<br>16.1 | 15.7 | 16 |
| 12-7 | 11.7 | 11.5 | 10.8 | 11 | 12.7 | 13.7 | 13.8 | 13 | 15.1 | 16.3<br>16.0 | 15.2 | 16 |
| 1-6-71 | 11.2 | 11.2 | 10.8 | 11 | 12.5 | 13.6 | 14.0 | 13 | 14.9 | 15.3<br>15.6 | 15.2 | 15 |
| 1-27 | 10.2 | 11.0 | 9.9 | 10 | 11.4 | 13.4 | 12.8 | 13 | 14.8 | 15.6<br>15.8 | 15.1 | 15 |
| 2-12 | 18.7 | 20.5 | 30.3 | 23 | 23.3 | 26.8 | 28.6 | 26 | 23.4 | 26.1<br>26.1 | 26.3 | 25 |
| 2-24 | 21.9 | 23.5 | 20.9 | 22 | 25.2 | 25.4 | 24.8 | 25 | 27.3 | 31.1<br>32.0 | 26.1 | 28 |
| 3-10 | 17.1 | 17.4 | 19.3 | 18 | 24.3 | 22.8 | 27.9 | 25 | 33.1 | 35.2<br>30.2 | 25.6 | 30 |
| 3-24 | 17.9 | 19.6 | 17.8 | 18 | 22.7 | 26.3 | 23.9 | 24 | 30.1 | 36.0<br>35.7 | 25.0 | 30 |
| 4-7 | 17.1 | 18.8 | 16.9 | 18 | 21.9 | 23.8 | 20.7 | 22 | 29.0 | 24.8<br>24.8 | 21.5 | 25 |
| 4-21 | 17.2 | 18.2 | 18.1 | 18 | 23.1 | 24.1 | 22.7 | 23 | 25.3 | 24.4<br>23.8 | 21.9 | 24 |
| 5-5 | 16.6 | 17.1 | 16.1 | 17 | 20.5 | 21.4 | 21.1 | 21 | 22.6 | 23.8<br>23.1 | 22.4 | 23 |
| 5-19 | 15.8 | 16.0 | 16.1 | 16 | 21.6 | 22.4 | 20.8 | 22 | 25.3 | 25.1<br>26.3 | 21.5 | 24 |

APPENDIX A

TABLE 2 (CONTD.)

| Plot | A-1 | | | | A-2 | | | | A-3 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sub-Sample | a | b | c | avg. | a | b | c | avg. | a | b | c | avg. |
| Date | | | | | | | | | | | | |
| 6-2-71 | 15.4 | 14.8 | 15.7 | 15 | 18.0 | 20.6 | 21.5 | 20 | 22.8 | 24.3<br>23.6 | 23.9 | 24 |
| 6-30 | 15.4 | 15.9 | 16.5 | 15 | 18.3 | 19.2 | 17.9 | 19 | 21.8 | 22.0<br>21.7 | 23.4 | 23 |
| 7-14 | 13.3 | 15.1 | 13.9 | 14 | 18.1 | 18.4 | 18.1 | 18 | 23.9 | 21.5<br>23.4 | 19.6 | 22 |
| 7-28 | 14.4 | 14.4 | 14.2 | 14 | 19.4 | 18.7 | 16.7 | 18 | 21.3 | 22.7<br>21.8 | 19.2 | 21 |
| 8-11 | 14.4 | 14.3 | 13.5 | 14 | 18.1 | 17.9 | 16.5 | 18 | 22.4 | 20.7<br>20.4 | 20.1 | 21 |
| 8-25 | 13.0 | 12.1 | 13.0 | 13 | 16.7 | 16.2 | 15.7 | 16 | 20.7 | 19.3<br>19.9 | 17.9 | 19 |
| 9-23 | 13.1 | 13.7 | 14.1 | 14 | 15.4 | 16.2 | 16.7 | 16 | 20.6 | 20.2<br>19.8 | 19.9 | 20 |
| 9-29 | 12.5 | 12.4 | 12.2 | 12 | 16.3 | 15.9 | 15.8 | 16 | 22.6 | 21.2 | 19.0 | 21 |

APPENDIX A

TABLE 3

OIL CONTENT OF INDIVIDUAL SOIL SAMPLES FOR "B" PLOTS
PERCENT WEIGHT

| Plot | B-1 | | | | B-2 | | | | B-3 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample Point | a | b | c | avg. | a | b | c | avg. | a | b | c | avg. |
| Date | | | | | | | | | | | | |
| 4-22-70 | 10.3 | 10.8<br>10.6 | 11.0 | 11 | 9.4 | 9.5 | 11.9 | 10 | 10.0 | 9.5 | 10.8 | 10 |
| 5-13 | 10.2 | 14.0 | 13.2 | 13 | 10.8 | 10.2<br>10.3 | 10.9 | 11 | 12.2 | 11.8 | 13.1 | 12 |
| 5-19 | 30.6 | 29.9 | 32.7 | 31 | 29.6 | 29.4 | 29.5 | 30 | 25.6 | 27.9<br>27.1 | 26.6 | 28 |
| 5-27 | 25.6 | 27.2<br>27.2 | 24.6 | 26 | 22.2 | 23.8 | 23.6 | 23 | 22.0 | 23.4 | 22.0 | 22 |
| 6-11 | 24.8 | 24.2 | 23.8 | 24 | 24.7 | 18.7 | 20.3 | 21 | 24.6 | 20.7 | 18.0 | 21 |
| 6-24 | 26.0 | 24.4 | 24.9 | 25 | 23.0 | 25.0 | 22.8 | 24 | 24.1 | 24.1 | 23.4 | 24 |
| 7-10 | 25.0 | 25.8 | 24.5 | 25 | 25.4 | 20.0 | 20.5 | 22 | 23.6<br>23.5 | 25.3 | 21.2 | 23 |
| 7-29 | 23.9 | 24.4 | 23.4 | 24 | 19.8 | 19.5<br>18.8 | 20.3 | 20 | 22.1 | 21.6 | 19.0 | 21 |
| 8-14 | 24.0 | 21.9 | 22.3 | 23 | 19.6 | 19.4 | 18.5 | 19 | 18.7 | 19.6<br>19.7 | 18.9 | 19 |
| 8-27 | 22.0 | 20.7 | 21.5 | 21 | 18.7 | 18.2 | 19.1 | 19 | 19.4 | 17.6<br>17.7 | 19.2 | 19 |
| 9-10 | 19.7 | 19.6 | 19.5 | 20 | 16.4 | 16.8 | 17.1 | 17 | 18.8 | 18.8<br>18.8 | 18.6 | 19 |
| 9-22 | 18.9 | 18.9 | -- | 19 | 16.6 | 16.6 | -- | 17 | 19.0 | 19.0 | -- | 19 |
| 10-16 | 17.5 | 16.6 | 17.9 | 17 | 15.8 | 15.5 | 15.4 | 16 | 19.1 | 18.5<br>17.5 | 18.8 | 19 |

APPENDIX A

TABLE 3 (CONTD.)

| Plot | B-1 | | | | B-2 | | | | B-3 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample Point | a | b | c | avg. | a | b | c | avg. | a | b | c | avg. |
| Date | | | | | | | | | | | | |
| 10-30-70 | 17.3 | 17.4 | 17.3 | 17 | 14.9 | 14.6 | 15.3 | 15 | 16.9 | 17.4<br>17.3 | 16.8 | 17 |
| 11-13 | 17.7 | 17.1 | 17.0 | 17 | 15.7 | 15.5 | 15.6 | 16 | 17.8 | 16.9<br>17.1 | 17.0 | 17 |
| 12-7 | 15.5 | 15.7 | 17.7 | 16 | 16.0 | 15.9 | 15.1 | 16 | 17.9 | 18.4<br>18.5 | 17.6 | 18 |
| 1-6-71 | 16.2 | 16.2 | 16.3 | 16 | 14.7 | 15.0 | 15.4 | 15 | 17.6 | 17.2<br>17.4 | 17.8 | 18 |
| 1-27 | 15.9 | 14.7 | 15.2 | 15 | 14.3 | 13.2 | 13.3 | 14 | 17.2 | 15.4<br>15.4 | 16.5 | 16 |
| 2-12 | 35.2 | 33.7 | 29.3 | 33 | 30.6 | 38.2 | 30.6 | 33 | 33.1 | 31.9<br>33.1 | 34.9 | 33 |
| 2-24 | 38.0 | 36.4 | 40.0 | 38 | 34.7 | 35.5 | 43.4 | 38 | 33.9 | 34.0<br>32.3 | 34.7 | 34 |
| 3-10 | 38.1 | 45.5 | 47.8 | 44 | 36.5 | 42.2 | 40.2 | 40 | 32.9 | 35.6<br>33.4 | 34.0 | 34 |
| 3-24 | 48.7 | 41.5 | 43.0 | 44 | 41.5 | 38.5 | 37.7 | 39 | 36.6 | 35.5<br>34.8 | 36.4 | 36 |
| 4-7 | 34.2 | 33.3 | 34.6 | 34 | 33.3 | 35.0 | 36.4 | 35 | 31.8 | 34.8<br>33.9 | 36.0 | 34 |
| 4-21 | 32.2 | 33.6 | 32.3 | 33 | 32.6 | 32.4 | 31.4 | 32 | 29.0 | 31.7<br>30.4 | 28.5 | 30 |
| 5-5 | 31.5 | 31.5 | 36.0 | 33 | 32.5 | 33.1 | 32.8 | 33 | 26.7 | 30.7<br>29.7 | 36.0 | 31 |
| 5-19 | 32.5 | 34.4 | 35.3 | 34 | 34.6 | 35.4 | 37.7 | 36 | 37.5 | 35.2<br>36.6 | 34.9 | 36 |

APPENDIX A

TABLE 3 (CONTD.)

| Plot | B-1 | | | | B-2 | | | | B-3 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample Point | a | b | c | avg. | a | b | c | avg. | a | b | c | avg. |
| Date | | | | | | | | | | | | |
| 6-2-71 | 37.6 | 37.3 | 31.3 | 35 | 36.3 | 36.2 | 38.7 | 37 | 35.6 | 29.8 | 28.5 | 31 |
| 6-30 | 33.2 | 31.9 | 30.0 | 32 | 36.4 | 38.8 | 34.0 | 36 | 33.0 | 31.2<br>36.1 | 33.3 | 33 |
| 7-14 | 34.8 | 32.2 | 31.0 | 33 | 35.7 | 37.6 | 39.1 | 38 | 33.5 | 36.1<br>35.3 | 28.5 | 33 |
| 7-28 | 36.2 | 34.2 | 26.9 | 32 | 38.6 | 36.5 | 31.8 | 36 | 31.1 | 30.4<br>31.1 | 32.2 | 31 |
| 8-11 | 28.9 | 31.7 | 32.4 | 31 | 26.6 | 25.7 | 29.5 | 27 | 34.8 | 30.4<br>30.9 | 29.6 | 32 |
| 8-25 | 29.6 | 29.2 | 28.9 | 29 | 30.0 | 20.8 | 21.6 | 24 | 34.3 | 29.7<br>26.8 | 31.9 | 32 |
| 9-23 | 29.1 | 25.9 | 22.6 | 26 | 30.6 | 19.9 | 22.2 | 24 | 26.4 | 25.5<br>26.2 | 26.7 | 26 |
| 9-29 | 24.2 | 25.4 | 25.7 | 25 | 25.4 | 24.1 | 22.0 | 24 | 31.2 | 26.8<br>28.1 | 32.0 | 30 |

## APPENDIX A

### TABLE 4

### OIL CONTENT OF INDIVIDUAL SOIL SAMPLES FOR "C" PLOTS
### PERCENT WEIGHT

| Plot | C-1 | | | | C-2 | | | | C-3 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample Point | a | b | c | avg. | a | b | c | avg. | a | b | c | avg. |
| Date | | | | | | | | | | | | |
| 4-22-70 | 9.4 | 10.5<br>10.7 | 10.6 | 10 | 9.4 | 9.6 | 9.6 | 10 | 10.6 | 9.9 | 10.3 | 10 |
| 5-13 | 10.6 | 11.9 | 13.2 | 11 | 9.5 | 12.2<br>12.4 | 13.8 | 12 | 9.0 | 12.1 | 12.6 | 11 |
| 5-19 | 23.4 | 23.0 | 24.2 | 24 | 16.7 | 20.8 | 22.6 | 20 | 17.3 | 18.1<br>18.3 | 20.5 | 19 |
| 5-27 | 20.3 | 23.0<br>22.8 | 23.1 | 22 | 18.5 | 22.9 | 24.6 | 22 | 18.3 | 19.1 | 19.5 | 19 |
| 6-11 | 21.6 | 21.7 | 22.7 | 22 | 16.2 | 20.5 | 22.6 | 20 | 17.4<br>17.2 | 19.8 | 20.5 | 19 |
| 6-24 | 19.2<br>19.3 | 20.4 | 16.4 | 19 | 12.8 | 16.0<br>15.8 | 18.3 | 16 | 15.5 | 18.7<br>18.6 | 17.4 | 17 |
| 7-10 | 17.3 | 17.2 | 25.6 | 20 | 24.3 | 18.1 | 22.4 | 22 | 15.4<br>15.5 | 18.8 | 17.8 | 17 |
| 7-29 | 16.9 | 19.1 | 21.5 | 19 | 16.7 | 18.2<br>16.7 | 20.1 | 18 | 15.6 | 17.9 | 19.2 | 18 |
| 8-14 | 17.4 | 18.5 | 19.1 | 18 | 16.9 | 15.7 | 19.3 | 17 | 15.4 | 17.1<br>17.2 | 17.8 | 17 |
| 8-27 | 14.8 | 17.4 | 18.4 | 17 | 12.8 | 13.5 | 18.2 | 15 | 14.2 | 16.7<br>16.8 | 16.1 | 16 |
| 9-10 | 15.8 | 15.5 | 15.8 | 16 | 14.2 | 14.3 | 12.8 | 14 | 14.4 | 14.4<br>14.3 | 15.4 | 15 |
| 9-22 | 14.2 | 14.2 | -- | 14 | 12.8 | 12.9 | -- | 13 | 15.3 | 15.2 | -- | 15 |

APPENDIX A

TABLE 4 (CONTD.)

| Plot | C-1 | | | | C-2 | | | | C-3 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample Point | a | b | c | avg. | a | b | c | avg. | a | b | c | avg. |
| Date | | | | | | | | | | | | |
| 10-16-70 | 12.8 | 14.6 | 15.1 | 14 | 10.9 | 13.1 | 15.3 | 13 | 13.8 | 16.3<br>16.8 | 16.4 | 16 |
| 10-30 | 11.5 | 11.7 | 13.1 | 12 | 13.2 | 12.2 | 14.8 | 13 | 12.7 | 14.5<br>14.9 | 14.0 | 14 |
| 11-13 | 12.1 | 13.8 | 13.8 | 13 | 10.9 | 13.5 | 11.7 | 12 | 13.0 | 14.0<br>14.5 | 13.2 | 13 |
| 12-7 | 11.2 | 14.1 | 14.7 | 13 | 10.5 | 11.8 | 13.4 | 12 | 12.8 | 14.4<br>14.7 | 14.2 | 14 |
| 1-6-71 | 11.8 | 13.2 | 13.7 | 13 | 10.8 | 12.6 | 13.0 | 12 | 12.5 | 14.3<br>14.7 | 14.6 | 14 |
| 1-27 | 11.2 | 12.5 | 12.1 | 12 | 10.4 | 12.4 | 13.7 | 12 | 12.9 | 14.1<br>14.0 | 14.5 | 14 |
| 2-12 | 27.8 | 30.9 | 32.9 | 31 | 29.5 | 26.5 | 30.9 | 29 | 24.0 | 26.3<br>26.7 | 31.3 | 27 |
| 2-24 | 29.8 | 32.6 | 37.3 | 33 | 29.8 | 29.5 | 33.2 | 31 | 25.9 | 28.9<br>27.9 | 30.1 | 28 |
| 3-10 | 27.7 | 25.9 | 32.2 | 29 | 31.0 | 29.9 | 29.8 | 30 | 26.7 | 28.6<br>27.2 | 30.5 | 29 |
| 3-24 | 23.9 | 26.7 | 28.9 | 27 | 24.7 | 27.9 | 28.9 | 27 | 26.4 | 27.5<br>27.8 | 29.9 | 28 |
| 4-7 | 22.1 | 27.4 | 25.9 | 25 | 24.7 | 26.4 | 27.0 | 26 | 25.4 | 26.5<br>26.6 | 28.9 | 27 |
| 4-21 | 21.1 | 25.9 | 24.6 | 24 | 26.2 | 24.6 | 25.4 | 25 | 24.5 | 25.6<br>25.8 | 28.9 | 26 |
| 5-5 | 21.7 | 26.7 | 23.6 | 24 | 24.6 | 26.6 | 25.9 | 26 | 24.9 | 25.7<br>25.8 | 27.9 | 26 |

## APPENDIX

TABLE 4 (CONTD.)

| Plot | C-1 | | | | C-2 | | | | C-3 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample Point | a | b | c | avg. | a | b | c | avg. | a | b | c | avg. |
| Date | | | | | | | | | | | | |
| 5-19-71 | 21.1 | 23.4 | 24.6 | 23 | 23.9 | 26.1 | 25.0 | 25 | 29.4 | 27.7<br>28.6 | 30.2 | 29 |
| 6-2 | 19.9 | 23.7 | 23.4 | 22 | 24.5 | 25.4 | 25.9 | 25 | 25.0 | 26.0 | 28.9 | 27 |
| 6-30 | 19.2 | 22.0 | 23.3 | 22 | 22.5 | 23.9 | 23.5 | 23 | 22.0 | 26.3<br>27.2 | 27.8 | 25 |
| 7-14 | 18.3 | 21.7 | 22.1 | 21 | 21.5 | 24.1 | 24.1 | 23 | 24.3 | 27.7<br>26.3 | 28.4 | 26 |
| 7-28 | 17.4 | 21.1 | 21.5 | 20 | 21.5 | 24.2 | 22.0 | 23 | 27.1 | 27.4<br>28.1 | 23.9 | 26 |
| 8-11 | 20.4 | 23.4 | 17.9 | 21 | 22.4 | 25.3 | 28.2 | 25 | 27.1 | 24.6<br>25 | 28.7 | 27 |
| 8-25 | 17.6 | 20.7 | 18.4 | 19 | 20.6 | 21.7 | 21.5 | 21 | 21.9 | 22.0<br>22.9 | 22.4 | 22 |
| 9-23 | 16.9 | 18.2 | 21.2 | 19 | 22.2 | 24.5 | 24.8 | 24 | 21.8 | 26.0<br>24.8 | 26.6 | 25 |
| 9-29 | 14.4 | 18.4 | 19.6 | 18 | 17.9 | 15.8 | 18.5 | 18 | 20.8 | 23.1<br>23.2 | 24.2 | 23 |

APPENDIX A

TABLE 5

CHRONOLOGICAL DATA

CRUDE OIL TANK BOTTOMS, "A" PLOTS

| | | 1970 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | APR. | MAY | | | | | JUNE | | JULY | | AUGUST | | |
| | | 22 | 7 | 13 | 17 | 19 | 27 | 11 | 24 | 10 | 29 | 7 | 14 | 27 |
| pH, Before Extr. | A-1 | 6.6 | | 7.3 | | | | 6.8 | | 7.0 | 7.3 | | 6.8 | |
| | A-2 | 6.9 | | 7.0 | | | | 6.8 | | 7.0 | | | 6.8 | |
| | A-3 | 6.8 | | 7.2 | | | | 6.8 | | 7.0 | | | 6.8 | |
| pH, After Extr. | A-1 | | | | | | | | | | | | | |
| | A-2 | | | | | | | | | | | | | |
| | A-3 | | | | | | | | | | | | | |
| Moisture, %w | A-1 | 11 | | 6 | | 17 | 20 | 12 | 8 | 18 | 9 | | 7 | 6 |
| | A-2 | 11 | | 6 | | 20 | 20 | 8 | 10 | 20 | 6 | | 7 | 7 |
| | A-3 | 12 | | 6 | | 19 | 20 | 8 | 10 | 17 | 6 | | 7 | 7 |
| Oil, %w | A-1 | 10 | | 10 | | 13 | 14 | 14 | 15 | 16 | 14 | | 14 | 13 |
| | A-2 | 11 | | 13 | | 16 | 16 | 17 | 17 | 17 | 16 | | 16 | 15 |
| | A-3 | 11 | | 13 | | 15 | 16 | 17 | 17 | 18 | 17 | | 17 | 17 |
| $NH_3$ as N, ppm | A-1 | Nil | | 720 | | | | 30 | | 30 | 3 | | 1525 | |
| | A-2 | Nil | | 220 | | | | 25 | | 20 | Nil | | 750 | |
| | A-3 | Nil | | Nil | | | | Nil | | Nil | Nil | | Nil | |
| $NO_3$ as N, ppm | A-1 | Nil | | Nil | | | | Nil | | 3 | Nil | | Nil | |
| | A-2 | Nil | | Nil | | | | Nil | | 1 | Nil | | Nil | |
| | A-3 | Nil | | Nil | | | | Nil | | Nil | Nil | | Nil | |
| $PO_4$ as $P_2O_5$, ppm | A-1 | 100 | | | | | | | | 240 | | | 320 | |
| | A-2 | | | | | | | | | 165 | | | 200 | |
| | A-3 | | | | | | | | | 95 | | | | |
| Temperature, °F | A-1 | 78 | 77 | 80 | | | 83 | 83 | 86 | | 89 | 89 | 94 | 94 |
| | A-2 | | | | | | | | | | | | | |
| | A-3 | | | | | | | | | | | | | |
| Ambient | | 80 | | 81 | | 80 | 82 | 82 | 76 | | 87 | 86 | 86 | 83 |
| Total Count Aerobes x $10^7$ | A-1 | | | 3 | | | | 170 | | 38 | | | 54 | |
| x $10^7$ | A-2 | | | 0.4 | | | | 190 | | 73 | | | 62 | |
| x $10^7$ | A-3 | | | 2 | | | | 10 | | 87 | | | 6 | |
| Number Plowings Between Sample Dates | | | | 1 | | 2 | 1 | 1 | 1 | 1 | 1 | | 2 | 1 |

Added urea and phosphorus

Added oil

Added urea and phosphorus

APPENDIX A

TABLE 5 (CONTD.)

CHRONOLOGICAL DATA

CRUDE OIL TANK BOTTOMS, "A" PLOTS

| | | 1970 | | | | | | 1971 | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | SEPT. | | OCT. | | NOV. | DEC. | JAN. | | FEB. | | | MARCH | | |
| | | 10 | 22 | 16 | 31 | 14 | 17 | 6 | 27 | 2 | 12 | 24 | 10 | 24 | |
| pH, Before Extr. | A-1 | 7.0 | 6.7 | 6.6 | | 6.7 | | | | | | | | | |
| | A-2 | 7.0 | 6.7 | 6.8 | | 6.9 | | | | | | | | | |
| | A-3 | 7.0 | 6.8 | 6.9 | | 7.0 | | | | | | | | | |
| pH, After Extr. | A-1 | | | | | | 6.2 | 6.3 | 6.5 | | 6.7 | | 6.6 | | |
| | A-2 | | | | | | 6.5 | 6.7 | 6.7 | | 6.9 | | 6.7 | | |
| | A-3 | | | | | | 6.8 | 6.7 | 6.8 | | 6.7 | | 6.9 | | |
| Moisture, %w | A-1 | 6 | 5 | 6 | 6 | 15 | 12 | 15 | 7 | Added oil | 23 | 10 | 20 | 10 | |
| | A-2 | 5 | 4 | 8 | 5 | 11 | 9 | 11 | 5 | | 22 | 15 | 17 | 9 | |
| | A-3 | 5 | 4 | 4 | 5 | 6 | 6 | 4 | 5 | | 23 | 20 | 20 | 12 | |
| Oil, %w | A-1 | 11 | 12 | 11 | 11 | 12 | 11 | 11 | 10 | | 23 | 22 | 18 | 18 | |
| | A-2 | 14 | 14 | 14 | 13 | 14 | 13 | 13 | 13 | | 26 | 25 | 25 | 24 | |
| | A-3 | 18 | 16 | 16 | 16 | 16 | 16 | 15 | 15 | | 25 | 28 | 31 | 30 | |
| $NH_3$ as N, ppm | A-1 | 565 | 500 | 540 | | Nil | 50 | 50 | Added $NH_4NO_3$ and Potash | | 390 | | 255 | | |
| | A-2 | 30 | 20 | 140 | | Nil | 40 | 10 | | | 260 | | 150 | | |
| | A-3 | Nil | Nil | Nil | | Nil | Nil | Nil | | | Nil | | Nil | | |
| $NO_3$ as N, ppm | A-1 | Nil | Nil | Nil | | Nil | Nil | Nil | | | 25 | | Nil | | |
| | A-2 | Nil | Nil | Nil | | Nil | Nil | Nil | | | Nil | | Nil | | |
| | A-3 | Nil | Nil | Nil | | Nil | Nil | Nil | | | Nil | | Nil | | |
| $PO_4$ as $P_2O_5$, ppm | A-1 | | | 720 | | 630 | 680 | 500 | 570 | | 540 | | | | |
| | A-2 | | | 370 | | 165 | 290 | 290 | 220 | | 200 | | | | |
| | A-3 | | | | | 85 | | 90 | 150 | | 130 | | | | |
| Temperature, °F | A-1 | 92 | 88 | 68 | 62 | 63 | 58 | 43 | 64 | 57 | 61 | 92 | 73 | 80 | |
| | A-2 | | | | | | | | 64 | 58 | 59 | 62 | 66 | 73 | |
| | A-3 | | | | | | | | 62 | 55 | 59 | 60 | 66 | 70 | |
| Ambient | | 82 | 83 | 62 | 65 | 60 | 61 | 38 | 60 | 43 | 58 | 65 | 70 | 58 | |
| Total Aerobes x $10^7$ | A-1 | | 48 | | 84 | 119 | 94 | 71 | | | 53 | | 77 | | |
| x $10^7$ | A-2 | | 40 | | 104 | 32 | 56 | 37 | | | 11 | | 52 | | |
| x $10^7$ | A-3 | | 7 | | 4 | 26 | 7 | 122 | | | 37 | | 6 | | |
| Number Plowings Between Sample Dates | | 5 | 0 | 3 | 3 | 3 | 5 | 2 | 3 | | 4 | 2 | 1 | 2 | |

APPENDIX A

TABLE 5 (CONTD.)

CHRONOLOGICAL DATA

CRUDE OIL TANK BOTTOMS, "A" PLOTS

| | | 1971 | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | APRIL | | MAY | | JUNE | | JULY | | AUGUST | | SEPT. | |
| | | 7 | 21 | 5 | 19 | 2 | 30 | 14 | 28 | 11 | 25 | 25 | 30 |
| pH, Before Extr. | A-1 | 6.2 | | | | | | | | 6.4 | | 6.8 | |
| | A-2 | 6.3 | | | | | | | | 6.5 | | 7.0 | |
| | A-3 | 6.7 | | | | | | | | 6.7 | | 7.3 | |
| pH, After Extr. | A-1 | | | 6.7 | | | 6.6 | 6.7 | | 6.7 | 7.0 | 6.9 | |
| | A-2 | | | 6.8 | | | 6.7 | 6.8 | | 6.8 | 7.1 | 7.1 | |
| | A-3 | | | 6.9 | | | 7.0 | 7.0 | | 6.9 | 7.3 | 7.2 | |
| Moisture, %w | A-1 | 6 | 11 | 6 | 7 | 5 | 16 | 10 | 12 | 21 | 5 | 16 | |
| | A-2 | 6 | 7 | 6 | 5 | 4 | 13 | 4 | 5 | 18 | 4 | 14 | |
| | A-3 | 8 | 7 | 6 | 7 | 6 | 15 | 6 | 6 | 15 | 4 | 12 | |
| Oil, %w | A-1 | 17 | 18 | 17 | 16 | 15 | 15 | 14 | 14 | 14 | 13 | 14 | 12 |
| | A-2 | 22 | 23 | 21 | 22 | 20 | 19 | 18 | 18 | 18 | 16 | 16 | 16 |
| | A-3 | 25 | 24 | 23 | 24 | 24 | 23 | 22 | 21 | 21 | 20 | 20 | 21 |
| $NH_3$ as N, ppm | A-1 | 120 | | 140 | | | 165 | 50 | | | 175 | 120 | |
| | A-2 | 85 | Added $NH_4NO_3$ | 60 | | | 80 | 25 | | Added $NH_4NO_3$ | 70 | 20 | |
| | A-3 | Nil | | Nil | | | Nil | Nil | | | Nil | Nil | |
| $NO_3$ as N, ppm | A-1 | 0 | | 30 | | | 25 | 5 | | | 65 | 20 | |
| | A-2 | 0 | | 10 | | | 10 | Nil | | | 40 | Nil | |
| | A-3 | 0 | | 0 | | | 0 | Nil | | | Nil | Nil | |
| $PO_4$ as $P_2O_5$, ppm | A-1 | 470 | | 470 | | | 500 | 580 | | 580 | 580 | 410 | |
| | A-2 | 210 | | 160 | | | 210 | 210 | | 210 | 210 | 200 | |
| | A-3 | 95 | | 95 | | | 95 | 95 | | 95 | 125 | 115 | |
| Temperature, °F | A-1 | 84 | 86 | 86 | 90 | 90 | 92 | 96 | 95 | 88 | 99 | 80 | |
| | A-2 | 88 | 89 | 87 | 98 | 90 | 94 | 94 | 93 | 92 | 96 | 82 | |
| | A-3 | 80 | 86 | 82 | 94 | 87 | 90 | 92 | 91 | 88 | 91 | 82 | |
| Ambient | | 67 | 75 | 80 | 82 | 83 | | 84 | 86 | 83 | 84 | 78 | |
| Total Aerobes x $10^7$ | A-1 | 16 | | | 100 | | 97 | 48 | | 58 | | | |
| x $10^7$ | A-2 | 10 | | | 30 | | 66 | 14 | | 59 | | | |
| x $10^7$ | A-3 | 0.5 | | | 1 | | 8 | 21 | | 35 | | | |
| Number Plowings Between Sample Dates | | 2 | 2 | 2 | 1 | 1 | 3 | 2 | 1 | 1 | 10 | | |

APPENDIX A

TABLE 6

CHRONOLOGICAL DATA

BUNKER C (NO. 6) FUEL OIL, "B" PLOTS

| | | 1970 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | APR. | MAY | | | | | JUNE | | JULY | | AUGUST | | |
| | | 22 | 7 | 13 | 17 | 19 | 27 | 11 | 24 | 10 | 29 | 7 | 14 | 27 |
| pH, Before Extr. | B-1 | 6.9 | | 7.3 | | | | 6.9 | | 7.1 | 7.5 | | 6.9 | |
| | B-2 | 7.0 | | 7.3 | | | | 6.9 | | 7.1 | | | 6.9 | |
| | B-3 | 7.0 | | 7.3 | | | | 7.0 | | 7.2 | | | 6.9 | |
| pH, After Extr. | B-1 | | | | | | | | | | | | | |
| | B-2 | | | | | | | | | | | | | |
| | B-3 | | | | | | | | | | | | | |
| Moisture, %w | B-1 | 12 | | 7 | | 6 | 7 | 7 | 5 | 14 | 4 | | 4 | 4 |
| | B-2 | 13 | | 7 | | 7 | 7 | 5 | 6 | 12 | 4 | | 4 | 4 |
| | B-3 | 11 | | 6 | | 8 | 9 | 6 | 6 | 13 | 6 | | 5 | 5 |
| Oil, %w | B-1 | 11 | Added urea and phosphorus | 13 | | 31 | 26 | 24 | 25 | 25 | 24 | Added urea and phosphorus | 23 | 21 |
| | B-2 | 10 | | 11 | | 30 | 23 | 21 | 24 | 22 | 20 | | 19 | 19 |
| | B-3 | 10 | | 12 | | 28 | 22 | 21 | 24 | 23 | 21 | | 19 | 19 |
| $NH_3$ as N, ppm | B-1 | Nil | | 980 | | | | 220 | | 140 | 10 | | 1100 | |
| | B-2 | Nil | | 700 | Added oil | | | 60 | | 15 | Nil | | 675 | |
| | B-3 | Nil | | Nil | | | | Nil | | Nil | Nil | | Nil | |
| $NO_3$ as N, ppm | B-1 | Nil | | Nil | | | | Nil | | Nil | Nil | | Nil | |
| | B-2 | Nil | | Nil | | | | Nil | | Nil | Nil | | Nil | |
| | B-3 | Nil | | Nil | | | | Nil | | Nil | Nil | | Nil | |
| $PO_4$ as $P_2O_5$, ppm | B-1 | 94 | | | | | | | | 180 | | | 770 | |
| | B-2 | | | | | | | | | 150 | | | 260 | |
| | B-3 | | | | | | | | | 105 | | | | |
| Temperature, °F | B-1 | 78 | 77 | 80 | | | 83 | 83 | 86 | | 89 | 89 | 94 | 94 |
| | B-2 | | | | | | | | | | | | | |
| | B-3 | | | | | | | | | | | | | |
| Ambient | | 80 | | 81 | | 78 | 82 | 82 | 76 | | 87 | 86 | 86 | 83 |
| Total Aerobes x $10^7$ | B-1 | | 1 | | | | | 10 | | 41 | | | 5 | |
| x $10^7$ | B-2 | | 1 | | | | | 12 | | 27 | | | 6 | |
| x $10^7$ | B-3 | | 0.6 | | | | | 5 | | 11 | | | 1 | |
| Number Plowings Between Sample Dates | | | | 1 | | 2 | 1 | 1 | 1 | 1 | 1 | | 2 | 1 |

APPENDIX A

TABLE 6 (CONTD.)

CHRONOLOGICAL DATA

BUNKER C (NO. 6) FUEL OIL, "B" PLOTS

| | | 1970 | | | | | | 1971 | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | SEPT. | | OCT. | | NOV. | DEC. | JAN. | | FEB. | | | MARCH | | |
| | | 10 | 22 | 16 | 31 | 14 | 17 | 6 | 27 | 2 | 12 | 24 | 10 | 24 | |
| pH, Before Extr. | B-1 | 7.0 | 6.6 | 6.5 | | 6.7 | | | | | | | | | |
| | B-2 | 7.1 | 6.8 | 6.7 | | 6.9 | | | | | | | | | |
| | B-3 | 7.0 | 6.9 | 6.9 | | 7.1 | | | | | | | | | |
| pH, After Extr. | B-1 | | | | | | 5.8 | 6.1 | 6.3 | | 6.4 | | 6.5 | | |
| | B-2 | | | | | | 6.3 | 6.5 | 6.5 | | 6.8 | | 6.8 | | |
| | B-3 | | | | | | 6.6 | 6.7 | 6.9 | Added Oil | 7.0 | | 6.9 | | |
| Moisture, %w | B-1 | 5 | 5 | 6 | 5 | 15 | 12 | 6 | 8 | | 8 | 8 | 9 | 8 | |
| | B-2 | 5 | 5 | 7 | 6 | 14 | 8 | 8 | 6 | | 9 | 8 | 9 | 8 | |
| | B-3 | 6 | 4 | 6 | 4 | 8 | 5 | 8 | 4 | | 8 | 7 | 9 | 9 | |
| Oil, %w | B-1 | 20 | 19 | 17 | 17 | 17 | 16 | 16 | 15 | | 33 | 33 | 33 | 33 | |
| | B-2 | 17 | 17 | 16 | 15 | 16 | 16 | 15 | 14 | | 33 | 33 | 33 | 33 | |
| | B-3 | 19 | 19 | 19 | 17 | 17 | 18 | 17 | 16 | | 33 | 33 | 33 | 33 | |
| $NH_3$ as N, ppm | B-1 | 655 | 420 | 220 | | Nil | 30 | 20 | | | 524 | | 634 | | |
| | B-2 | 55 | 35 | 195 | | Nil | 20 | 10 | | | 412 | | 254 | | |
| | B-3 | Nil | Nil | Nil | | Nil | Nil | Nil | | | Nil | | Nil | | |
| $NO_3$ as N, ppm | B-1 | Nil | Nil | Nil | | Nil | Nil | Nil | Added $NH_4NO_3$ and Potash | | 110 | | 50 | | |
| | B-2 | Nil | Nil | Nil | | Nil | Nil | Nil | | | 120 | | 35 | | |
| | B-3 | Nil | Nil | Nil | | Nil | Nil | Nil | | | Nil | | Nil | | |
| $PO_4$ as $P_2O_5$, ppm | B-1 | | | 800 | | 920 | 1100 | 900 | 1125 | | 1160 | | 825 | | |
| | B-2 | | | 360 | | | 285 | 275 | 270 | | 300 | | 210 | | |
| | B-3 | | | | | | 175 | 130 | 140 | | 140 | | 110 | | |
| Temperature, °F | B-1 | 92 | 88 | 68 | 62 | 63 | 58 | 43 | 68 | 58 | 59 | 60 | 68 | 69 | |
| | B-2 | | | | | | | | 64 | 56 | 59 | 62 | 70 | 68 | |
| | B-3 | | | | | | | | 59 | 54 | 59 | 62 | 74 | 68 | |
| Ambient | | 82 | 83 | 62 | 65 | 60 | 61 | 38 | 60 | 43 | 58 | 65 | 70 | 58 | |
| Total Aerobes x $10^7$ | B-1 | | 37 | | 155 | 80 | 73 | 210 | | | 3 | | | | |
| x $10^7$ | B-2 | | 28 | | 27 | 75 | 18 | 21 | | | 2 | | | | |
| x $10^7$ | B-3 | | 3 | | 3 | 27 | 3 | 53 | | | 3 | | 3 | | |
| Number Plowings Between Sample Dates | | 5 | 0 | 3 | 3 | 3 | 5 | 2 | 3 | | 4 | 2 | 1 | 2 | |

APPENDIX A

TABLE 6 (CONTD.)

CHRONOLOGICAL DATA

BUNKER C (NO. 6) FUEL OIL, "B" PLOTS

| | | 1971 | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | APRIL | | MAY | | JUNE | | JULY | | AUGUST | | SEPT. | |
| | | 7 | 21 | 5 | 19 | 2 | 30 | 14 | 28 | 11 | 25 | 25 | 30 |
| pH, Before Extr. | B-1 | 6.6 | | | | | | | | 6.3 | | 6.8 | |
| | B-2 | 6.8 | | | | | | | | 6.5 | | 7.0 | |
| | B-3 | 6.9 | | | | | | | | 6.7 | | 7.2 | |
| pH, After Extr. | B-1 | | | 6.9 | | | 6.9 | 6.9 | | 6.5 | 7.1 | 6.9 | |
| | B-2 | | | 6.9 | | | 7.0 | 7.0 | | 6.6 | 7.2 | 7.0 | |
| | B-3 | | | 7.0 | | | 7.1 | 7.1 | | 6.7 | 7.3 | 7.2 | |
| Moisture, %w | B-1 | 9 | 6 | 6 | 3 | 3 | 5 | 3 | 3 | 6 | 2 | 4 | |
| | B-2 | 7 | 8 | 6 | 3 | 3 | 5 | 2 | 3 | 6 | 2 | 6 | |
| | B-3 | 9 | 9 | 7 | 3 | 3 | 4 | 2 | 3 | 6 | 2 | 4 | |
| Oil, %w | B-1 | 34 | 33 | 33 | 34 | 35 | 32 | 33 | 32 | 31 | 29 | 26 | 25 |
| | B-2 | 35 | 32 | 33 | 36 | 37 | 36 | 38 | 36 | 27 | 24 | 24 | 22 |
| | B-3 | 34 | 30 | 31 | 36 | 31 | 33 | 33 | 31 | 32 | 32 | 26 | 30 |
| $NH_3$ as N, ppm | B-1 | 630 | | 440 | | | 410 | 360 | | | 430 | 116 | |
| | B-2 | 370 | | 300 | | | 290 | 170 | | | 230 | Nil | |
| | B-3 | Nil | Added $NH_4NO_3$ | Nil | | | Nil | Nil | | Added $NH_4NO_3$ | Nil | Nil | |
| $NO_3$ as N, ppm | B-1 | 20 | | 100 | | | 20 | 15 | | | 145 | Nil | |
| | B-2 | Nil | | 5 | | | 1 | 1 | | | 125 | Nil | |
| | B-3 | Nil | | Nil | | | Nil | Nil | | | Nil | Nil | |
| $PO_4$ as $P_2O_5$, ppm | B-1 | 930 | | 750 | | | 840 | 900 | | 800 | 740 | 680 | |
| | B-2 | 240 | | 220 | | | 230 | 230 | | 230 | 250 | 230 | |
| | B-3 | 100 | | 100 | | | 80 | 95 | | 95 | 130 | 115 | |
| Temperature, °F | B-1 | 90 | 94 | 85 | 102 | 92 | 96 | 93 | 94 | 90 | 95 | 82 | |
| | B-2 | 96 | 92 | 84 | 103 | 92 | 94 | 95 | 93 | 90 | 95 | 81 | |
| | B-3 | 93 | 87 | 83 | 101 | 92 | 92 | 93 | 93 | 88 | 94 | 81 | |
| Ambient | | 67 | 75 | 80 | 82 | 83 | | 84 | 86 | 83 | 84 | 78 | |
| Total Aerobes x $10^7$ | B-1 | 5 | | | 4 | | 3 | 5 | | 54 | | | |
| x $10^7$ | B-2 | 0.1 | | | 10 | | 2 | 4 | | 30 | | | |
| x $10^7$ | B-3 | 0.1 | | | 30 | | 3 | 1 | | 0.5 | | | |
| Number Plowings Between Sample Dates | | 2 | 2 | 2 | 1 | 1 | 3 | 2 | 1 | 1 | 10 | | |

APPENDIX A

TABLE 7

CHRONOLOGICAL DATA

WAXY OIL PRODUCT, "C" PLOTS

| | | 1970 | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | APR. | MAY | | | | | JUNE | | JULY | | AUGUST | | | |
| | | 22 | 7 | 13 | 17 | 19 | 27 | 11 | 24 | 10 | 29 | 7 | 14 | 27 | |
| pH, Before Extr. | C-1 | 7.0 | | 7.4 | | | | 6.8 | | 7.2 | 7.5 | | 6.9 | | |
| | C-2 | 7.0 | | 7.7 | | | | 6.8 | | 7.2 | | | 6.9 | | |
| | C-3 | 7.0 | | 7.4 | | | | 6.9 | | 7.2 | | | 6.8 | | |
| pH, After Extr. | C-1 | | | | | | | | | | | | | | |
| | C-2 | | | | | | | | | | | | | | |
| | C-3 | | | | Added oil | | | | | | | | | | |
| Moisture, %w | C-1 | 17 | | 8 | | 17 | 9 | 8 | 9 | 16 | 6 | | 6 | 6 | |
| | C-2 | 17 | | 7 | | 15 | 8 | 8 | 8 | 13 | 6 | | 5 | 6 | |
| | C-3 | 13 | | 7 | | 16 | 10 | 8 | 9 | 12 | 8 | | 5 | 5 | |
| Oil, %w | C-1 | 10 | | 11 | | 24 | 22 | 22 | 19 | 20 | 19 | | 18 | 17 | |
| | C-2 | 10 | | 12 | | 20 | 22 | 20 | 16 | 22 | 18 | | 17 | 15 | |
| | C-3 | 10 | | 11 | | 19 | 19 | 19 | 17 | 17 | 18 | | 17 | 16 | |
| $NH_3$ as N, ppm | C-1 | Nil | | 440 | | | | 50 | | 40 | 3 | | 1230 | | |
| | C-2 | Nil | | 520 | | | | 30 | | 35 | Nil | | 770 | | |
| | C-3 | Nil | | Nil | | | | Nil | | Nil | Nil | | Nil | | |
| $NO_3$ as N, ppm | C-1 | Nil | | Nil | | | | Nil | | Nil | Nil | | Nil | | |
| | C-2 | Nil | | Nil | | | | Nil | | Nil | Nil | | Nil | | |
| | C-3 | Nil | | Nil | | | | Nil | | Nil | Nil | | Nil | | |
| $PO_4$ as $P_2O_5$, ppm | C-1 | 110 | | | | | | | | 140 | | | 470 | | |
| | C-2 | | | | | | | | | 105 | | | 160 | | |
| | C-3 | | | | | | | | | 80 | | | | | |
| Temperature, °F | C-1 | 78 | 77 | 80 | | | 83 | 83 | 86 | | 89 | 89 | 94 | 94 | |
| | C-2 | | | | | | | | | | | | | | |
| | C-3 | | | | | | | | | | | | | | |
| Ambient | | 80 | | 81 | | 80 | 82 | 82 | 76 | | 87 | 86 | 86 | 83 | |
| Total Aerobes x $10^7$ | C-1 | | 4 | | | | | 16 | | 39 | | | 31 | | |
| x $10^7$ | C-2 | | 5 | | | | | 41 | | 128 | | | 25 | | |
| x $10^7$ | C-3 | | 2 | | | | | 10 | | 45 | | | 4 | | |
| Number Plowings Between Sample Dates | | | | 1 | | 2 | 1 | 1 | 1 | 1 | 1 | | 2 | 1 | |

Added urea and phosphorus

Added urea and phosphorus

APPENDIX A

TABLE 7 (CONTD.)

CHRONOLOGICAL DATA

WAXY OIL PRODUCT, "C" PLOTS

| | | 1970 | | | | | | 1971 | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | SEPT. | | OCT. | | NOV. | DEC. | JAN. | | FEB. | | | MARCH | |
| | | 10 | 22 | 16 | 31 | 14 | 17 | 6 | 27 | 2 | 12 | 24 | 10 | 24 |
| pH, Before Extr. | C-1 | 7.0 | 6.6 | 6.5 | | 6.7 | | | | | | | | |
| | C-2 | 7.0 | 6.9 | 6.7 | | 6.9 | | | | | | | | |
| | C-3 | 7.0 | 7.0 | 7.0 | | 7.1 | | | | | | | | |
| pH, After Extr. | C-1 | | | | | | 6.2 | 6.2 | 6.4 | | 6.6 | | 6.7 | |
| | C-2 | | | | | 6.6 | 6.6 | 6.6 | 6.7 | | 7.0 | | 6.9 | |
| | C-3 | | | | | 7.0 | 7.0 | 7.0 | 6.9 | | 6.9 | | 7.1 | |
| Moisture, %w | C-1 | 5 | 4 | 7 | 7 | 10 | 6 | 8 | 8 | Added Oil | 10 | 9 | 12 | 13 |
| | C-2 | 5 | 4 | 7 | 9 | 8 | 6 | 7 | 6 | | 11 | 10 | 12 | 10 |
| | C-3 | 6 | 4 | 5 | 7 | 10 | 5 | 6 | 5 | | 9 | 8 | 9 | 5 |
| Oil, %w | C-1 | 16 | 15 | 14 | 12 | 13 | 13 | 13 | 12 | | 31 | 33 | 29 | 27 |
| | C-2 | 14 | 13 | 13 | 13 | 12 | 12 | 12 | 12 | | 29 | 31 | 30 | 27 |
| | C-3 | 15 | 15 | 16 | 14 | 13 | 14 | 14 | 14 | | 27 | 28 | 29 | 28 |
| $NH_3$ as N, ppm | C-1 | 380 | 180 | 115 | | Nil | 20 | 20 | | | 460 | | 460 | |
| | C-2 | 65 | 20 | 10 | | Nil | 5 | 10 | | | 310 | | 290 | |
| | C-3 | Nil | Nil | Nil | | Nil | Nil | Nil | | | Nil | | Nil | |
| $NO_3$ as N, ppm | C-1 | Nil | Nil | Nil | | Nil | Nil | Nil | Added $NH_4NO_3$ and Potash | | 40 | | 15 | |
| | C-2 | Nil | Nil | Nil | | Nil | Nil | Nil | | | 30 | | 13 | |
| | C-3 | Nil | Nil | Nil | | Nil | Nil | Nil | | | Nil | | Nil | |
| $PO_4$ as $P_2O_5$, ppm | C-1 | | | 720 | | 700 | 780 | 880 | 780 | | 720 | | 650 | |
| | C-2 | | | 360 | | 320 | 295 | 270 | 280 | | 250 | | 210 | |
| | C-3 | | | | | 135 | | 125 | 140 | | 150 | | 105 | |
| Temperature, °F | C-1 | 92 | 88 | 68 | 62 | 63 | 58 | 43 | 64 | 57 | 59 | 82 | 68 | 70 |
| | C-2 | | | | | | | | 62 | 55 | 58 | 63 | 68 | 82 |
| | C-3 | | | | | | | | 60 | 53 | 58 | 63 | 68 | 70 |
| Ambient | | 82 | 83 | 62 | 65 | 60 | 61 | 38 | 60 | 43 | 58 | 65 | 70 | 58 |
| Total Aerobes x $10^7$ | C-1 | | 74 | | 87 | 110 | 49 | 80 | | | 17 | | 34 | |
| x $10^7$ | C-2 | | 44 | | 19 | 93 | 34 | 66 | | | 7 | | 41 | |
| x $10^7$ | C-3 | | 67 | | 10 | 38 | 7 | 15 | | | 4 | | 130 | |
| Number Plowings Between Sample Dates | | 5 | 0 | 3 | 3 | 3 | 5 | 2 | 3 | | 4 | 2 | 1 | 2 |

APPENDIX A

TABLE 7 (CONTD.)

CHRONOLOGICAL DATA

WAXY OIL PRODUCT, "C" PLOTS

| | | 1971 | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | APRIL | | MAY | | JUNE | | JULY | | AUGUST | | SEPT. | |
| | | 7 | 21 | 5 | 19 | 2 | 30 | 14 | 28 | 11 | 25 | 25 | 30 |
| pH, Before Extr. | C-1 | | | | | | | | | 6.3 | | 6.7 | |
| | C-2 | | | | | | | | | 6.3 | | 7.2 | |
| | C-3 | | | | | | | | | 6.6 | | 7.0 | |
| pH, After Extr. | C-1 | 6.2 | | 6.6 | | | 6.8 | 6.8 | | 6.5 | 6.9 | 6.8 | |
| | C-2 | 6.5 | | 6.7 | | | 7.0 | 6.9 | | 6.6 | 7.1 | 6.9 | |
| | C-3 | 6.8 | | 6.9 | | | 7.2 | 7.1 | | 6.9 | 7.3 | 7.2 | |
| Moisture, %w | C-1 | 4 | 7 | 4 | 9 | 4 | 13 | 5 | 6 | 13 | 3 | 12 | |
| | C-2 | 4 | 7 | 4 | 8 | 5 | 14 | 6 | 5 | 13 | 3 | 11 | |
| | C-3 | 4 | 5 | 4 | 3 | 4 | 9 | 4 | 5 | 8 | 3 | 8 | |
| Oil, %w | C-1 | 25 | 24 | 24 | 23 | 22 | 21 | 21 | 20 | 21 | 19 | 19 | 18 |
| | C-2 | 26 | 25 | 26 | 25 | 25 | 23 | 23 | 23 | 25 | 21 | 24 | 18 |
| | C-3 | 27 | 26 | 26 | 29 | 27 | 25 | 26 | 26 | 27 | 22 | 25 | 23 |
| $NH_3$ as N, ppm | C-1 | 325 | | 205 | | 120 | 230 | 110 | | | 225 | Nil | |
| | C-2 | 120 | | 65 | | 40 | 130 | 35 | | | 70 | Nil | |
| | C-3 | Nil | | Nil | | Nil | Nil | Nil | | | Nil | Nil | |
| $NO_3$ as N, ppm | C-1 | Nil | | 90 | | Nil | 2 | Nil | | | 60 | Nil | |
| | C-2 | Nil | | 20 | | Nil | 2 | Nil | | | 50 | Nil | |
| | C-3 | Nil | | Nil | | Nil | Nil | Nil | | | Nil | Nil | |
| $PO_4$ as $P_2O_5$, ppm | C-1 | 750 | | 620 | | | 620 | 780 | | 780 | 775 | 550 | |
| | C-2 | 260 | | 180 | | | 200 | 280 | | 300 | 320 | 260 | |
| | C-3 | 110 | | 90 | | | 90 | 90 | | 90 | 130 | 115 | |
| Temperature, °F | C-1 | 88 | 94 | 86 | 97 | 92 | 96 | 98 | 96 | 94 | 99 | 84 | |
| | C-2 | 82 | 86 | 86 | 94 | 90 | 92 | 94 | 94 | 92 | 98 | 82 | |
| | C-3 | 80 | 82 | 82 | 90 | 86 | 90 | 92 | 92 | 91 | 92 | 83 | |
| Ambient | | 67 | 75 | 80 | 82 | 83 | | 84 | 86 | 83 | 84 | 78 | |
| Total Aerobes x $10^7$ | C-1 | 4 | | | 10 | | 4 | 19 | | 42 | | | |
| x $10^7$ | C-2 | 1 | | | 10 | | 49 | 20 | | 50 | | | |
| x $10^7$ | C-3 | 0.1 | | | 9 | | 135 | 10 | | 10 | | | |
| Number Plowings Between Sample Dates | | 2 | 2 | 2 | 1 | 1 | 3 | 2 | 1 | 1 | 10 | | |

Added $NH_4NO_3$

Added $NH_4NO_3$

APPENDIX A

TABLE 8

TOTAL NITROGEN, SULFUR, PHOSPHORUS, AND METALS CONTENTS FOR "A" PLOTS

Legend: Solvent a was 1.0 N Ammonium Acetate, pH 7, used for soil analysis at Texas A&M University.
Solvent b was 1.4 N Ammonium Acetate in 1 N HCl, at pH 4.2[9] and the analyses were by atomic absorption.

| Component in ppm | START April, 1970 | | Plot No. | DURING Nov. 13, 1970 | DURING April 21, 1971 | END Sept. 23, 1971 | |
|---|---|---|---|---|---|---|---|
| | Total | | | Total | Total | Total | |
| Nitrogen | 1500 | | A-1 | 2820 | | 3300 | |
| | 1300 | | | 2500 | | 3100 | |
| | 1600 | | A-2 | 2590 | | 3600 | |
| | | | | | | 3200 | |
| | | | A-3 | 1650 | | 2100 | |
| | | | | | | 1800 | |
| Sulfur | 5000 | | A-1 | | | 2300 | |
| | | | A-2 | | | 2500 | |
| | | | A-3 | | | 3400 | |
| | | EXTRACTABLE WITH SOLVENT | | | EXTRACTABLE WITH SOLVENT | | EXTRACTABLE WITH SOLVENT |
| | | a b | | | b | b | a b |
| Phosphorus | 820 | 36 | A-1 | 3000 | | 500 | 98 |
| | | | A-2 | | | 370 | 36 |
| | | | A-3 | | | 430 | 21 |
| Sodium | | 45 700 | A-1 | | 96 | 350 | 352 260 |
| | | | A-2 | | 146 | 1000 | 560 260 |
| | | | A-3 | | 88 | 510 | 550 360 |
| Potassium | | 156 930 | A-1 | | 140 | 600 | 586 920 |
| | | | A-2 | | 140 | 375 | 460 920 |
| | | | A-3 | | 140 | 210 | 236 740 |
| Magnesium | | 1490 2050 | A-1 | | 1100 | 6850 | 560 5750 |
| | | | A-2 | | 1300 | 6700 | 600 7250 |
| | | | A-3 | | 1400 | 6700 | 560 7120 |
| Calcium | | 3300 26900 | A-1 | | 45000 | 27500 | 5900 24800 |
| | | | A-2 | | 21000 | 26500 | 7300 28000 |
| | | | A-3 | | 22000 | 26250 | 6550 28000 |

APPENDIX A

TABLE 8 (CONTD.)

TOTAL NITROGEN, SULFUR, PHOSPHORUS, AND METALS CONTENTS FOR "A" PLOTS

Legend: Solvent c was 1 N HCl used for soil analysis at Texas A&M University.
Solvent d was a 50/50 mixture HCl and $HNO_3$ and the analyses were by atomic absorption.

| Component in ppm | START April, 1970 | | Plot No. | DURING Nov. 13, 1970 | DURING April 21, 1971 | END Sept. 23, 1971 | |
|---|---|---|---|---|---|---|---|
| | EXTRACTABLE WITH SOLVENT c | EXTRACTABLE WITH SOLVENT d | | EXTRACTABLE WITH SOLVENT d | EXTRACTABLE WITH SOLVENT d | EXTRACTABLE WITH SOLVENT c | EXTRACTABLE WITH SOLVENT d |
| Manganese | 692 | 160 | A-1 | 260 | 160 | 146 | 210 |
| | | | A-2 | 200 | 270 | 146 | 180 |
| | | | A-3 | 270 | 130 | 144 | 240 |
| Iron | 3800 | 10000 | A-1 | 9750 | 16500 | 1110 | 21500 |
| | | | A-2 | 10000 | 20000 | 1160 | 21500 |
| | | | A-3 | 11500 | 19800 | 1230 | 25300 |
| Zinc | 1580 | 1080 | A-1 | 1000 | 1200 | 685 | 1200 |
| | | | A-2 | 1140 | 1560 | 595 | 1500 |
| | | | A-3 | 1150 | 1640 | 628 | 1220 |
| Copper | 21 | 180 | A-1 | 150 | 180 | 37 | 170 |
| | | | A-2 | 160 | 230 | 42 | 160 |
| | | | A-3 | 160 | 200 | 45 | 170 |
| Lead | - | - | A-1 | 820 | 890 | - | 880 |
| | | | A-2 | 900 | 980 | - | 790 |
| | | | A-3 | 920 | 1030 | - | 920 |

APPENDIX A

TABLE 9

TOTAL NITROGEN, SULFUR, PHOSPHORUS, AND METALS CONTENTS FOR "B" PLOTS

Legend: Solvent a was 1.0 N Ammonium Acetate, pH 7, used for soil analysis at Texas A&M University.
Solvent b was 1.4 N Ammonium Acetate in 1 N HCl, at pH 4.2[9] and the analyses were by atomic absorption.

| Component in ppm | START April, 1970 | | Plot No. | DURING Nov. 13, 1970 | | DURING April 21, 1971 | | END Sept. 23, 1971 | |
|---|---|---|---|---|---|---|---|---|---|
| | Total | | | Total | | Total | | Total | |
| Nitrogen | 1500 | | B-1 | 3050 | | | | 3300 | |
| | 1300[e] | | | | | | | 3000 | |
| | 1600[f] | | B-2 | | | | | 3300 | |
| | | | | | | | | 3600 | |
| | | | B-3 | | | | | 2400 | |
| | | | | | | | | 2000 | |
| Sulfur | 5000 | | B-1 | 5000 | | | | 4000 | |
| | | | B-2 | | | | | 3800 | |
| | | | B-3 | | | | | 5300 | |
| | | EXTRACTABLE WITH SOLVENT | | | EXTRACTABLE WITH SOLVENT | | EXTRACTABLE WITH SOLVENT | | EXTRACTABLE WITH SOLVENT |
| | | a b | | | b | | b | | a b |
| Phosphorus | 820 | 36 | B-1 | 3810 | | | | 970 | 222 |
| | | | B-2 | | | | | 280 | 35 |
| | | | B-3 | | | | | 360 | 16 |
| Sodium | | 45 700 | B-1 | | 100 | | 500 | | 270 220 |
| | | | B-2 | | | | 330 | | 238 210 |
| | | | B-3 | | | | 300 | | 278 220 |
| Potassium | | 156 930 | B-1 | | 140 | | 550 | | 796 920 |
| | | | B-2 | | | | 375 | | 484 520 |
| | | | B-3 | | | | 210 | | 258 520 |
| Magnesium | | 1490 2050 | B-1 | | 1000 | | 6850 | | 550 6250 |
| | | | B-2 | | | | 6250 | | 490 6750 |
| | | | B-3 | | | | 6850 | | 550 7120 |
| Calcium | | 3300 26900 | B-1 | | 17000 | | 29000 | | 5200 24440 |
| | | | B-2 | | | | 25000 | | 5550 26440 |
| | | | B-3 | | | | 27250 | | 5900 25200 |

APPENDIX A

TABLE 9 (CONTD.)

TOTAL NITROGEN, SULFUR, PHOSPHORUS, AND METALS CONTENTS FOR "B" PLOTS

Legend: Solvent c was 1 N HCl used for soil analysis at Texas A&M University.
Solvent d was a 50/50 mixture HCl and $HNO_3$ and the analyses were by atomic absorption.

| Component in ppm | START April, 1970 | | Plot No. | DURING Nov. 13, 1970 | DURING April 21, 1971 | END Sept. 23, 1971 | |
|---|---|---|---|---|---|---|---|
| | EXTRACTABLE WITH SOLVENT c | EXTRACTABLE WITH SOLVENT d | | EXTRACTABLE WITH SOLVENT d | EXTRACTABLE WITH SOLVENT d | EXTRACTABLE WITH SOLVENT c | EXTRACTABLE WITH SOLVENT d |
| Manganese | 692 | 160 | B-1 | 180 | 130 | 138 | 180 |
| | | | B-2 | | 140 | 138 | 190 |
| | | | B-3 | | 150 | 150 | 160 |
| Iron | 3800 | 10000 | B-1 | 6250 | 16500 | 1140 | 22600 |
| | | | B-2 | | 20500 | 960 | 22600 |
| | | | B-3 | | 21800 | 980 | 37600 |
| Zinc | 1580 | 1080 | B-1 | 850 | 1700 | 387 | 1250 |
| | | | B-2 | | 1640 | 376 | 1090 |
| | | | B-3 | | 1460 | 349 | 860 |
| Copper | 21 | 180 | B-1 | 130 | 200 | 10 | 170 |
| | | | B-2 | | 200 | 22 | 150 |
| | | | B-3 | | 180 | 28 | 150 |
| Lead | - | - | B-1 | 780 | 1090 | - | 1000 |
| | | | B-2 | | 1150 | - | 880 |
| | | | B-3 | | 1230 | - | 830 |

## APPENDIX A

### TABLE 10

### TOTAL NITROGEN, SULFUR, PHOSPHORUS, AND METALS CONTENTS FOR "C" PLOTS

Legend: Solvent a was 1.0 N Ammonium Acetate, pH 7, used for soil analysis at Texas A&M University.
Solvent b was 1.4 N Ammonium Acetate in 1 N HCl, at pH 4.2[9] and the analyses were by atomic absorption.

| Component in ppm | START April, 1970 | | Plot No. | DURING Nov. 13, 1970 | DURING April 21, 1971 | END Sept. 23, 1971 | |
|---|---|---|---|---|---|---|---|
| | Total | | | Total | Total | Total | |
| Nitrogen | 1500 | | C-1 | | | 4200 | |
| | 1300 | | | | | 3500 | |
| | 1600 | | C-2 | 2600 | | 3000 | |
| | | | | | | 2500 | |
| | | | C-3 | 1690 | | 1900 | |
| | | | | | | 1900 | |
| Sulfur | 5000 | | C-1 | 3500 | | 2700 | |
| | | | C-2 | | | 2200 | |
| | | | C-3 | | | 2200 | |
| | | EXTRACTABLE WITH SOLVENT | | | EXTRACTABLE WITH SOLVENT | | EXTRACTABLE WITH SOLVENT |
| | | a | b | | b | b | | a | b |
| Phosphorus | 820 | 36 | | C-1 | | | 940 | 134 | |
| | | | | C-2 | | | 280 | 38 | |
| | | | | C-3 | | | 120 | 15 | |
| Sodium | | 45 | 700 | C-1 | - | 260 | | 240 | 180 |
| | | | | C-2 | 60 | 280 | | 246 | 220 |
| | | | | C-3 | 59 | 420 | | 206 | 220 |
| Potassium | | 156 | 930 | C-1 | - | 600 | | 792 | 800 |
| | | | | C-2 | 140 | 440 | | 554 | 720 |
| | | | | C-3 | 140 | 250 | | 225 | 580 |
| Magnesium | | 1490 | 2050 | C-1 | - | 6525 | | 500 | 6250 |
| | | | | C-2 | 1200 | 6525 | | 630 | 7120 |
| | | | | C-3 | 1400 | 6250 | | 590 | 7500 |
| Calcium | | 3300 | 26900 | C-1 | - | 27250 | | 5200 | 22800 |
| | | | | C-2 | 20000 | 26750 | | 6200 | 22000 |
| | | | | C-3 | 22000 | 27000 | | 6600 | 29600 |

APPENDIX A

TABLE 10 (CONTD.)

TOTAL NITROGEN, SULFUR, PHOSPHORUS, AND METALS CONTENTS FOR "C" PLOTS

Legend: Solvent c was 1 N HCl used for soil analysis at Texas A&M University.
Solvent d was a 50/50 mixture HCl and $HNO_3$ and the analyses were by atomic absorption.

| Component in ppm | START April, 1970 | | Plot No. | DURING Nov. 13, 1970 | DURING April 21, 1971 | END Sept. 23, 1971 | |
|---|---|---|---|---|---|---|---|
| | EXTRACTABLE WITH SOLVENT c | EXTRACTABLE WITH SOLVENT d | | EXTRACTABLE WITH SOLVENT d | EXTRACTABLE WITH SOLVENT d | EXTRACTABLE WITH SOLVENT c | EXTRACTABLE WITH SOLVENT d |
| Manganese | 692 | 160 | C-1 | - | 100 | 180 | 260 |
| | | | C-2 | 210 | 220 | - | 250 |
| | | | C-3 | 200 | 1000 | 162 | 200 |
| Iron | 3800 | 10000 | C-1 | - | 15500 | 980 | 21300 |
| | | | C-2 | 11250 | 20000 | - | 22300 |
| | | | C-3 | 12500 | 20800 | 830 | 23000 |
| Zinc | 1580 | 1080 | C-1 | - | 1180 | 842 | 920 |
| | | | C-2 | 900 | 1560 | - | 1190 |
| | | | C-3 | 900 | 1260 | 441 | 1150 |
| Copper | 21 | 180 | C-1 | - | 150 | 18 | 140 |
| | | | C-2 | 140 | 170 | - | 140 |
| | | | C-3 | 150 | 170 | 48 | 140 |
| Lead | - | - | C-1 | - | 1030 | - | 900 |
| | | | C-2 | 860 | 1110 | - | 820 |
| | | | C-3 | 940 | 1020 | - | 880 |

APPENDIX A

TABLE 11

OIL AND NUTRIENT PENETRATION DEPTHS INTO SOIL

| | | | A | | | B | | | C | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 |
| OIL | | | | | | | | | | | |
| 0 - 0.5 ft. | | Start | 10 | 13 | 13 | 13 | 11 | 12 | 11 | 12 | 11 |
| | | Midway | 10 | 13 | 15 | 15 | 14 | 16 | 12 | 12 | 14 |
| | | End | 12 | 16 | 21 | 25 | 24 | 30 | 18 | 18 | 23 |
| 2 ft. | | Start | 8 | 18 | 21 | 11 | 11 | 11 | 11 | 11 | 11 |
| | | Midway | 6 | 11 | 13 | 11 | 11 | 16 | 12 | 11 | 16 |
| | | End | 7 | 21 | 25 | 15 | 13 | 12 | 13 | 12 | 18 |
| 4 ft. | | Start | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 |
| | | Midway | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 |
| | | End | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 |
| 6 ft. | | Start | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 |
| | | Midway | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 |
| | | End | — | — | — | — | — | — | — | — | — |
| NUTRIENT | | | | | | | | | | | |
| $NH_3$, 2 ft. | | Midway | NIL | | | 96 | | | NIL | | |
| | | End | — | | NIL | NIL | | | NIL | | |
| 4 ft. | | Midway | NIL | | | NIL | | | NIL | | |
| | | End | — | | NIL | NIL | | | NIL | NIL | |
| $NO_3$, 2 ft. | | Midway | NIL | | | NIL | | | NIL | | |
| | | End | — | | NIL | NIL | | | NIL | | |
| 4 ft. | | Midway | NIL | | | NIL | | | NIL | | |
| | | End | — | | NIL | NIL | | | | 50 | |
| $P_2O_5$, 2 ft. | | Midway | 240 | | | 160 | | | 190 | | |
| | | End | — | | 150 | 150 | | | 200 | | |
| 4 ft. | | Midway | NIL | | | NIL | | | NIL | NIL | |
| | | End | — | | NIL | NIL | | | — | | |

APPENDIX A

TABLE 12

HYDROCARBON TYPE FOR "A" PLOTS

| | | Percent Weight | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Basis Oil | | | | Basis Soil | | | |
| | | Sats. | Resin | Arom. | Total | Sats. | Resin | Arom. | Total |
| **AT START** | | | | | | | | | |
| Residual oil in soil | A-1 | 40 | 21 | 39 | 100 | 4.0 | 2.1 | 3.9 | 10 |
| | A-2 | 40 | 21 | 39 | 100 | 5.2 | 2.7 | 5.1 | 13 |
| | A-3 | 40 | 21 | 39 | 100 | 5.2 | 2.7 | 5.1 | 13 |
| Oil added | | 36 | 8 | 56 | 100 | | | | |
| After addition (calculated) | A-1 | | | | | 6.2 | 2.6 | 7.3 | 17 |
| | A-2 | | | | | 7.0 | 3.1 | 7.9 | 18 |
| | A-3 | | | | | 7.0 | 3.1 | 7.9 | 18 |
| **AFTER 8 MONTHS** | | | | | | | | | |
| Residual oil in soil | A-1 | 16 | 50 | 32 | 100 | 1.8 | 5.5 | 3.5 | 11 |
| | A-2 | 27 | 29 | 44 | 100 | 3.5 | 3.8 | 5.8 | 13 |
| | A-3 | 33 | 34 | 33 | 100 | 5.3 | 5.4 | 5.3 | 16 |
| Oil added | | 44 | 5 | 51 | 100 | | | | |
| After addition (calculated) | A-1 | | | | | 6.3 | 6.1 | 8.6 | 21 |
| | A-2 | | | | | 9.2 | 4.5 | 12.4 | 26 |
| | A-3 | | | | | 10.6 | 6.0 | 11.4 | 28 |
| **AFTER 14 MONTHS** | | | | | | | | | |
| Residual oil in soil | A-1 | 24 | 32 | 44 | 100 | 3.8 | 5.1 | 7.1 | 16 |
| | A-2 | 30 | 22 | 48 | 100 | 6.3 | 4.6 | 10.2 | 21 |
| | A-3 | 35 | 18 | 47 | 100 | 8.4 | 4.3 | 11.3 | 24 |
| **AT END (17 MONTHS)** | | | | | | | | | |
| Residual oil in soil | A-1 | 14 | 44 | 42 | 100 | 1.7 | 5.3 | 5.0 | 12 |
| | A-2 | 21 | 42 | 37 | 100 | 3.1 | 6.3 | 5.6 | 15 |
| | A-3 | 35 | 26 | 39 | 100 | 6.3 | 4.7 | 7.0 | 18 |

APPENDIX A

TABLE 13

HYDROCARBON TYPE FOR "B" PLOTS

| | | Percent Weight | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Basis Oil | | | | Basis Soil | | | |
| | | Sats. | Resin | Arom. | Total | Sats. | Resin | Arom. | Total |
| AT START | | | | | | | | | |
| Residual oil in soil | B-1 | 40 | 21 | 39 | 100 | 5.2 | 2.7 | 5.1 | 13 |
| | B-2 | 40 | 21 | 39 | 100 | 4.4 | 2.3 | 4.3 | 11 |
| | B-3 | 40 | 21 | 39 | 100 | 4.8 | 2.5 | 4.7 | 12 |
| Oil added | | 18 | 26 | 56 | 100 | | | | |
| After addition (calculated) | B-1 | | | | | 7.9 | 6.6 | 13.5 | 28 |
| | B-2 | | | | | 6.9 | 5.9 | 12.0 | 25 |
| | B-3 | | | | | 7.0 | 5.6 | 11.4 | 25 |
| AFTER 8 MONTHS | | | | | | | | | |
| Residual oil in soil | B-1 | 10 | 39 | 51 | 100 | 1.7 | 6.6 | 8.7 | 17 |
| | B-2 | 15 | 36 | 49 | 100 | 2.1 | 5.0 | 6.9 | 14 |
| | B-3 | 26 | 25 | 49 | 100 | 4.4 | 4.3 | 8.3 | 17 |
| Oil added | | 21 | 27 | 52 | 100 | | | | |
| After addition (calculated) | B-1 | | | | | 6.3 | 12.6 | 20.1 | 39 |
| | B-2 | | | | | 7.4 | 11.7 | 19.9 | 39 |
| | B-3 | | | | | 8.2 | 9.2 | 17.7 | 35 |
| AFTER 14 MONTHS | | | | | | | | | |
| Residual oil in soil | B-1 | 14 | 29 | 57 | 100 | 4.3 | 9.0 | 17.7 | 31 |
| | B-2 | 13 | 23 | 65 | 100 | 4.2 | 7.4 | 20.8 | 32 |
| | B-3 | 21 | 23 | 56 | 100 | 6.7 | 7.4 | 17.9 | 32 |
| AT END (17 MONTHS) | | | | | | | | | |
| Residual oil in soil | B-1 | 13 | 40 | 47 | 100 | 3.3 | 10.0 | 11.7 | 25 |
| | B-2 | 17 | 33 | 50 | 100 | 4.6 | 8.9 | 13.5 | 27 |
| | B-3 | 23 | 26 | 51 | 100 | 6.9 | 7.8 | 15.3 | 30 |

APPENDIX A

TABLE 14

HYDROCARBON TYPE FOR "C" PLOTS

| | | Percent Weight | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Basis Oil | | | | Basis Soil | | | |
| | | Sats. | Resin | Arom. | Total | Sats. | Resin | Arom. | Total |
| **AT START** | | | | | | | | | |
| Residual oil in soil | C-1 | 40 | 21 | 39 | 100 | 4.4 | 2.3 | 4.3 | 11 |
| | C-2 | 40 | 21 | 39 | 100 | 4.8 | 2.5 | 4.7 | 12 |
| | C-3 | 40 | 21 | 39 | 100 | 4.4 | 2.3 | 4.3 | 11 |
| Oil added | | 90 | Nil | 10 | 100 | | | | |
| After addition (calculated) | C-1 | | | | | 15.2 | 2.3 | 5.5 | 23 |
| | C-2 | | | | | 12.9 | 2.5 | 5.6 | 21 |
| | C-3 | | | | | 11.6 | 2.3 | 5.1 | 19 |
| **AFTER 8 MONTHS** | | | | | | | | | |
| Residual oil in soil | C-1 | 27 | 35 | 38 | 100 | 3.5 | 4.6 | 4.9 | 13 |
| | C-2 | 38 | 26 | 36 | 100 | 4.6 | 3.1 | 4.3 | 12 |
| | C-3 | 42 | 23 | 35 | 100 | 5.9 | 3.2 | 4.9 | 14 |
| Oil added | | 90 | Nil | 10 | 100 | | | | |
| After addition (calculated) | C-1 | | | | | 18.8 | 4.6 | 6.6 | 30 |
| | C-2 | | | | | 19.9 | 3.1 | 6.0 | 29 |
| | C-3 | | | | | 18.5 | 3.2 | 6.3 | 28 |
| **AFTER 14 MONTHS** | | | | | | | | | |
| Residual oil in soil | C-1 | 51 | 19 | 30 | 100 | 11.7 | 4.4 | 6.9 | 23 |
| | C-2 | 60 | 14 | 26 | 100 | 14.4 | 3.4 | 6.2 | 24 |
| | C-3 | 62 | 10 | 28 | 100 | 16.1 | 2.6 | 7.3 | 26 |
| **AT END (17 MONTHS)** | | | | | | | | | |
| Residual oil in soil | C-1 | 34 | 33 | 33 | 100 | 5.8 | 5.6 | 5.6 | 17 |
| | C-2 | 54 | 18 | 28 | 100 | 11.3 | 3.8 | 5.9 | 21 |
| | C-3 | 61 | 13 | 26 | 100 | 14.6 | 3.1 | 6.3 | 24 |

# APPENDIX B

## MICROBIAL ANALYSES

### PROCEDURE

Soil sample was mixed thoroughly and one gram was weighed aseptically and placed in a dilution bottle containing 99 ml saline. The sample was shaken vigorously for one minute then placed on a rotary shaker for 25 minutes. At the end of this period the bottle was removed and one ml was pipetted into another 90 ml saline blank and mixed 30 seconds. One-tenth ml of this sample was pipetted onto the surface of a nutrient agar plate and spread with a sterile glass spreader. Further serial dilutions and platings were made of the sample in order to obtain statistically accurate plates (those with 30-300 colonies). Duplicate platings were made of each sample.

After four days' incubation at 30°C the plates were counted, and the four most numerous organisms were isolated for identification. Gram strains and normal biochemical tests were performed on the isolates and identification was made through Bergey's Manual of Determinative Bacteriology.[6]

Predominant individual organisms determined monthly throughout the project for "A", "B", and "C" plots are given in following Tables 1, 2, and 3, respectively. A brief description from literature[3,6] of each predominant organism follows these tables.

APPENDIX B

TABLE 1

PREDOMINANT INDIVIDUAL ORGANISMS FOR "A" PLOTS

LEGEND

a = A-1
b = A-2
c = A-3

| | 1970 | | | | | | | | | | | | 1971 | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| MICROORGANISM | MAY | JUNE | JULY | AUG. | SEPT. | OCT. | NOV. | DEC. | JAN. | FEB. | MAR. | APR. | MAY | JUNE | JULY | AUG. | SEPT. |
| Achromobacter, Sp | | | | | | a | | | | | b | | | | | b | |
| cycloclastes | | | | c | | | | | | | | | | | | | |
| delmarvae | | | | | | | | | | c | | | | | | | |
| pestifer | | | | | | | | | | | | | | | | | |
| xerosis | | c | | | | | | | | | | | | | | | |
| Arthrobacter, Sp | | | | | | | | | | | | | | | | | |
| tumescens | abc | abc | ac | a | abc | | ac | bc | | | | | | ab | | | |
| Bacillus, Sp | | | | | | | | a | | | | | | | | | |
| cereus var.mycoides | | | | | | | | | | | | | | | | | |
| Corynebacterium, Sp | | | | | ab | | bc | a | c | bc | acc | | bcc | abc | aabc | | |
| Flavobacterium, Sp | | | | abc | | abcc | | | bc | | ab | abc | bc | | a | a | |
| aquatile | | | a | | | | | | | | | | | | | | |
| arborescens | | | | | | | | | | | | | | | | | |
| balustinum | bc | b | | | | | | | | | | | | | | | |
| breve | | | | | | | | | | | | | | | | | |
| diffusum | | | | | | | | | | | | | | | | | |
| ferrugineum | | | bc | | | | | | | | | | | | | | a |
| lutescens | ab | | | | | | | | | | | | a | ac | | | |
| peregrinum | c | | | c | | | | | | | | | | | | | |
| rhenanum | | | | | | | | | | | | | | | | | |
| rigense | | b | | | | | | | | | | | | | | | |
| solare | | | | | | | | | ac | | | | | | | b | c |
| Micrococcus, Sp | | | | | | | abc | | | | | | | | c | | a |
| roseus | | | | | | | | | | | | | | | | | |

APPENDIX B

TABLE 1 (CONTD.)

PREDOMINANT INDIVIDUAL ORGANISMS FOR "A" PLOTS

| MICROORGANISM | 1970 MAY | JUNE | JULY | AUG. | SEPT. | OCT. | NOV. | DEC. | 1971 JAN. | FEB. | MAR. | APR. | MAY | JUNE | JULY | AUG. | SEPT. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Nocardia, Sp | | | | | | | b | a | | | | | | | | | |
| actinomorpha | | | | | | | | | | | | | | | | | |
| alba | | | | | c | | | | b | | | | | | | c | |
| corallina | | ac | ab | b | | c | | | | | | | | | | | bc |
| flavescens | | | | | | bc | | | | | | | | | | | |
| maculata | | | | | | | | | | abc | | | | | | | |
| minima | | | | | bc | | | | ab | bc | ac | | | bc | | ac | |
| opaca | | | bc | a | | | | | | | | | | | | | |
| paraffinae | | | | | | | | ac | a | | | | | | | | |
| polychromogenes | | | | ab | | ab | | | | | | | | | | | |
| rubroportincta | | | | | | | | | | | | | | | | | |
| salmonicolor | | | | | | | ac | | | | | | | | | | |
| Pseudomonas, Sp | | c | | a | | | | | bc | a | ab | abc | abc | b | abc | c | c |
| aeruginosa | a | | | | | | | | | | | abcc | | | | | |
| arvilla | c | | | | | | | | | | | | | | | | |
| boreopolis | | | | | | | | | | | | | | | | | |
| crucivlae | | | | | | | ab | abc | | | | | | | | | ab |
| dacunhae | | | | | | | | | | | | | | | | | |
| denitrificans | | | | | | | | | | | | | | | | | |
| effusa | | | c | | | | | | | | | | | | | | |
| oleovorans | | | | | | | | | | | | | | | | | |
| ovalis | | | | | | | | | | ab | | | | ac | | a | |
| putida | | | | | | | | | | | | ab | ab | | | | |
| rathonis | | | | | | | | | | | | | | | | | |
| striata | | | b | | | | | | b | | | | | | | | |
| stutzeri | | ab | a | | | | | | | | | | | | | | |
| Rhodotorula, Sp | b | a | | | | | | | | | | | a | | | | |
| Saccharomyces, Sp | | | | b | abc | b | | bbc | | | | | | | | b | |
| analatus | | | | | | | | | | | | | | | | | |
| Sarcina, Sp | | | | b | | | | | | | | | | | | | |
| barkeri | a | | | | | | | | | | | | | | | | |
| flava | | | | | | | | | | | | | | | | | |
| Yeast | | | | | | | | | | | bc | | | | bbc | abc | abbc |

## APPENDIX B

### TABLE 2

### PREDOMINANT INDIVIDUAL ORGANISMS FOR "B" PLOTS

LEGEND

a = B-1
b = B-2
c = B-3

| MICROORGANISM | 1970 MAY | JUNE | JULY | AUG. | SEPT. | OCT. | NOV. | DEC. | 1971 JAN. | FEB. | MAR. | APR. | MAY | JUNE | JULY | AUG. | SEPT. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Achromobacter, Sp | | | | | ab | a | | a | | | | c | | | | | |
| cycloclastes | a | b | | | | | c | | | | | | | | | | |
| delmarvae | | | | | | | | | | | | | | | | | |
| pestifer | | b | | | | | | | | | | | | | | | |
| xerosis | | | | | | | | | | | | | | | | | |
| Arthrobacter, Sp | | | | | | | | | | | | | | | | | |
| tumescens | bc | ac | a | abc | ab | | a | ac | | | b | | | | | | |
| Bacillus, Sp | | | | | | | | | | | | | | | | | |
| cereus var.mycoides | | | | | | | | | | | | | a | | | | |
| Corynebacterium, Sp | | | | | bc | | bc | bbc | abc | c | b | a | abc | abc | abc | aac | aabb |
| Flavobacterium, Sp | | c | c | bcc | | cc | ab | | bc | | b | ac | | b | b | b | |
| aquatile | | | | | | | | | | | | | | | | | |
| arborescens | | | | | | | | | | | | | | | | | |
| balustinum | | | b | | | | | | | | | | | | | | |
| breve | | | c | | | | | | | | | | | | | | |
| diffusum | | | bc | | | ac | | | | | | | | | | | |
| ferrugineum | bc | | a | | | bc | | | | a | | | | | | b | |
| lutescens | b | | | | | | | | | b | | | | | | | bc |
| peregrinum | c | | abc | | | ab | | | | | a | | | | | | |
| rhenanum | — | a | | | | | | | | | | | | | | | |
| rigense | | | | | | | | | | | | | | | | | |
| solare | | a | | | | | | | a | | | | | bc | ac | ac | |
| Micrococcus, Sp | a | | | | | | bcc | | abc | | c | | b | | | | |
| roseus | | | | | | | | | | | | | | | | | |

APPENDIX B

TABLE 2 (CONTD.)

PREDOMINANT INDIVIDUAL ORGANISMS FOR "B" PLOTS

| | 1970 | | | | | | | | 1971 | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| MICROORGANISM | MAY | JUNE | JULY | AUG. | SEPT. | OCT. | NOV. | DEC. | JAN. | FEB. | MAR. | APR. | MAY | JUNE | JULY | AUG. | SEPT. |
| Nocardia, Sp | | | | | | | | | | | | | | | | | |
| actinomorpha | | | | | | | | | | c | | | | | | | |
| alba | | | | | | | | | | | | | | | | | |
| corallina | | ac | a | | | b | | | | | | | | | | | |
| flavescens | | | | | | b | | | | | | | | | | | |
| maculata | | | | | | | | | | | | | | | | | |
| minima | | | | | abc | | | | | abc | | | | ac | | a | |
| opaca | | | b | a | | | | | | | | | | | | | |
| paraffinae | | | | ab | | | | | b | | | | c | | | c | |
| polychromogenes | | | | b | | | | | | | c | | | | | | |
| rubroportincta | | | | | | | | | | | | | | | | | |
| salmonicolor | | | | | | | | abc | | | | | bc | ab | | | c |
| Pseudomonas, Sp | | | | | | | | | | | ab | abc | c | ac | aac | | ac |
| aeruginosa | | bc | | | | | | | | | | abbc | | | | | |
| arvilla | | | | | | | | | | ab | | b | a | | | | |
| boreopolis | | | | | | | | | | | | | | | | | |
| crucivlae | | | | | | | a | | | | | | | | | | c |
| dacunhae | | | | | | | | abc | | | | | | | | | |
| denitrificans | | | | | | | ab | | | | c | | | | | | |
| effusa | | | | | | | | | | | | | | | | | |
| oleovorans | | | | | a | | | | | | | | | | | | |
| ovalis | | | | | | | | | | | | | | | | c | |
| putida | | b | | | | | | | | | | | | | | | |
| rathonis | | | | | | | | | | | | | | | | | |
| striata | | | | b | | a | | | a | | a | | | | | | |
| stutzeri | | | | | | | | | | | | | | | | | |
| Rhodotorula, Sp | abc | | | | | | | | | | | | a | | | c | |
| Saccharomyces, Sp | | | | | c | | | | c | abc | | | | | | | |
| analatus | | | | | | | | | | | | | | | | | |
| Sarcina, Sp | | | | | | | | | | | | | b | | | | |
| barkeri | | | | | | | | | | | | | | | | | |
| flava | | | | | c | | | | | | | | | | | | |
| Yeast | | | | | | | | | | | ac | | | | bbc | b | ab |

APPENDIX B

TABLE 3

PREDOMINANT INDIVIDUAL ORGANISMS FOR "C" PLOTS

LEGEND

a = C-1
b = C-2
c = C-3

| MICROORGANISM | 1970 | | | | | | | | 1971 | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | MAY | JUNE | JULY | AUG. | SEPT. | OCT. | NOV. | DEC. | JAN. | FEB. | MAR. | APR. | MAY | JUNE | JULY | AUG. | SEPT. |
| Achromobacter, Sp. | | | | | a | c | | c | | | | | | | | | |
| cycloclastes | | a | | | | | | ac | | | | | | | | | |
| delmarvae | | | | | | | | | | | | | | | | | |
| pestifer | | | c | | | | | | | | | | | | | | |
| xerosis | | | | | | | | | | | | | | | | | |
| Arthrobacter, Sp | | | | | | | | | | | | | | | | | |
| tumescens | c | | ab | ab | bc | | | a | | | | | | | | | |
| Bacillus, Sp | | | | | | | | | a | c | | | | | | | |
| cereus var.mycoides | | | | | | | | | | | | | | | | | |
| Corynebacterium, Sp | | | | | | | a | b | bc | abc | bc | | bb | ab | bc | a | bc |
| Flavobacterium, Sp | | cc | bc | bcc | | abc | c | a | abcc | | b | a | | | c | abc | |
| aquatile | b | | | | | c | | | | | | | | | | | |
| arborescens | | | | | | | | | | | | | | | | | |
| balustinum | | | | | | | | | | | | | | | | | |
| breve | | | | | | | | | | | | | | | | | |
| diffusum | | ab | c | | | | | | | | | | | | | | |
| ferrugineum | | | a | | | | | | | | | | | | | c | |
| lutescens | | | | | | | | | | | | | | | | | |
| peregrinum | | | | c | | | | | | | | | | | | | |
| rhenanum | | c | | | | | | | | | | | | | | | |
| rigense | | | | | | | | | | | | | | | | | |
| solare | | | | | | | | | ac | | | | | | | | |
| Micrococcus, Sp | | | | | | | b | b | | | a | | a | abc | | | a |
| roseus | | c | | | | | | | | | | | | | | | |

APPENDIX B

TABLE 3 (CONTD.)

PREDOMINANT INDIVIDUAL ORGANISMS FOR "C" PLOTS

| MICROORGANISM | 1970 MAY | JUNE | JULY | AUG. | SEPT. | OCT. | NOV. | DEC. | 1971 JAN. | FEB. | MAR. | APR. | MAY | JUNE | JULY | AUG. | SEPT. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Nocardia, Sp | | | | | | | | | | | | | a | | | c | |
| actinomorpha | | | | | | | c | | ab | | | | | | | a | |
| alba | | | | | b | | | | | | | | | | | | |
| corallina | | | a | | | | | | | | | | | | | | |
| flavescens | | | | a | | abc | | | | | | | | | | | |
| maculata | | | | | | | | | | | | | | | | | |
| minima | | | | | a | | | | | ac | | | b | | | b | a |
| opaca | | | bc | | | | | | | | | | | | | | |
| paraffinae | | | | ab | bc | | bc | | b | | c | | b | b | a | | |
| polychromogenes | | | | b | c | ab | | b | | b | | | | | | | |
| rubroportincta | | | | a | | | | | | | | | | | | | |
| salmonicolor | | | | | | | | | | | abc | | | | c | | |
| Pseudomonas, Sp | a | | | | | | | b | ab | | | aabbc | a | abcc | ab | bc | |
| aeruginosa | | ab | | | | | | | | | | abbcc | | | | | |
| arvilla | a | | | | | | | | | ac | | c | | | | | |
| boreopolis | a | | | | | | | | | | | | | | | | |
| crucivlae | c | | | | | | a | | | | | | | | | | |
| dacunhae | | b | | | | | | c | | | | | | | | | |
| denitrificans | | | | | a | | | | | | | | | | | | |
| effusa | | | | | | | | | | | | | | | | | |
| oleovorans | ab | b | b | c | | | | | | | b | | | | | | |
| ovalis | | | a | | | | | | | b | | | | | a | | |
| putida | | | | | | | | | | | | | a | ac | | | ac |
| rathonis | b | | | | | | | | | | | | | | | | |
| striata | | | | | | | | | | | | | | | | | |
| stutzeri | | | | | | | | | | | | | | | | | |
| Rhodotorula, Sp | c | a | | | | | | | | | | | | | | | |
| Saccharomyces, Sp | | | | | abc | ab | aab | ac | | | | | | | | | |
| analatus | | | | | | | | | | | | | | | | | |
| Sarcina, Sp | | | | | | | c | | | | | | cccc | | | | |
| barkeri | | | | | | | | | | | | | | | | | |
| flava | | | | | | | | | | | aac | | | | abbc | ab | abbbcc |
| Yeast | | | | | | | | | | | | | | | | | |

APPENDIX B

MICROBIAL ANALYSES

BRIEF DESCRIPTION OF PREDOMINANT ORGANISMS

| | |
|---|---|
| Achromobacterium, Sp | Attacks polysulfide polymer and found in used oil[3] |
| cycloclastes | Attack phenol and naphthalene, organic acids not formed[6] |
| delmarvae | Produces acid from glucose, nitrites from nitrates[6] |
| pestifer | Organic acids from hydrocarbons not formed[6] |
| xerosis | Produces nitrites from nitrates[6] |
| Arthrobacter, Sp | |
| tumescens | Citrates not utilized, nitrates and ammonia not sole source of N[6] |
| Azotobacter, Sp | Fixes atmospheric nitrogen, gives off $CO_2$, opt temp 25-28C[6] |
| agilis | |
| Bacillus, Sp | Attacks polysulfide polymers, found in jet air fuel, utilize paraffins but not cycloparaffins[3] |
| cereus var.mycoides | Optimum pH 5.2, temp 40°C, starch, sugar hydrolizes and produces acetylmethylcarbonol[6] |
| Corynebacterium, Sp | Seldom produces acid, glucose reacts to $CO_2$ + $H_2O$[6], utilizes paraffin tetradecane[3] |
| Flavobacterium, Sp | Acids not developed when nitrogen containing compounds are in the medium[6] |
| aquatile | pH 6.5 - 7.8, 10-30°C, produce acid from sugar[6] |
| arborescens | Opt temp 30°C[6] survive in jet fuel[3] |
| balustinum | 20-25°C[6], |
| breve | 35° found in sewage[6] |
| diffusum | 25-30°C[6], attacks polysulfide polymer[3] |
| ferrugineum | pH 7-7.5 min. 6.5, 22-39°C, decomposes carbohydrates[6] |
| lutescens | 30-35°C |
| peregrinum | Opens benzene rings, destroys 2,4 dichlorophenoxyacetic acid[6] |

| | |
|---|---|
| rhenanum | 30°C produces acid from sugar, no reaction with starch[6] |
| rigense | 30°C produces acid from glucose and starch hydrolized[6] |
| solare | 30°C |
| Hyphomicrobium, Sp | |
| vulgare | pH 7-7.5, 20-37°C, utilizes organic acids[6] |
| Micrococcus, Sp | Utilizes paraffins, oxidizes phenols and found in used oil[3] |
| roseus | 25°C |
| Nocardia, Sp | Highly efficient paraffin to cellular matter conversion[3] |
| actinomorpha | pH 7.8 - 8.5, 25-30°C, utilizes phenols and naphthalene[6], oxidizes alkyl cyclic hydrocarbon[6] |
| alba | Hydrolizes sugar, starch and organic acids[6] |
| corallina | pH 6.8 - 8, 22-25°C, utilizes phenol, cresol, and naphthol[6] |
| florescens | 28-38°C, hydrolizes starch[6] |
| maculata | Hydrolizes starch[6] |
| minima | 22-25°C, utilizes paraffin[6] |
| opaca | pH 6.8 - 7.3, 30°C, utilizes phenol and naphthalene[6] |
| paraffinae | Min. pH 4.4, utilizes paraffin wax[6] |
| polychromogenos | 22-25°C[6] |
| rubropertineta | pH 6.8 - 7.2, 20-37°C, utilizes benzene, paraffin and mix petroleum[6] |
| salmonicolor | 20-22°C, utilizes paraffins[6] |
| Pseudomonas, Sp | Oxidizes paraffins, cycloparaffins, hydrocarbons, used oil[3], oxidizes hydrocarbons[6] |
| aeruginesa | 37-42°C, oxidizes toluene, asphalt, produces odor trimethylamine (TMA)[6] |
| arvilla | 37°C, attacks naphthalene[6] |
| boreopolis | 35-37°C, attacks naphthalene[6] |
| crucivlae | 30-35°C, attacks phenols and m-cresol[6] |
| dacunhae | 37°C, attacks phenols[6] |
| denitrificans | 25°C[6] |
| effusa | 37°C[6] |

| | |
|---|---|
| olevorans | 25-37°C, attacks cutting oil and starch[6] |
| ovalis | 25-36°C[6] |
| putida | 25-27°C, putrify material and form TMA[6] |
| rathonis | 35°C, attacks phenol, cresol and naphthalene[6] |
| striata | 25-36°C[6] |
| stutzeri | pH 7-9, 35°C, anaerobic $NO_3$ to N[6] |
| Rhodotorula, Sp | |
| Saccharomyces, Sp | |
| analatus | |
| Sarcina, Sp | Found in used oil[3] |
| barkeri | pH 7, 30°C, produces methane from carbonic acid[6] |
| flava | |
| Streptomyces, Sp | Utilize paraffins and found in used oil[3] |
| anulutus | Antagonistic mycobacteria |
| bikiniensis | Strongly antagonistic, produces streptomycin |
| Yeast | |

## APPENDIX C

## MICROBIOLOGY CONSULTANT'S COMMENTS

Many studies have been carried out on the identity of organisms capable of oxidizing hydrocarbons. The results obtained in this project are very similar to the results obtained in other research projects.[15] The major species present are members of the genus Pseudomonas, Flavobacterium, Nocardia, Corynebacterium, and Arthrobacter.

The nature of the hydrocarbon substrate does not appear to influence the types of organisms present; however, it does have an effect upon the number of bacteria in the soil samples. Generally, the same types of organisms predominated in the three plots. Crude oil tank bottom sludge produced the highest counts, the waxy oil product produced intermediate counts, while bunker C fuel exhibited the lowest microbial population.

Some evidence of ecological progression was noted during the 18-month test period. Members of the genera Achromobacter and Arthrobacter were present in the early stages of the project but gradually disappeared from the plots. These genera were generally absent from all plots during the second half of the study. Members of genus Corynebacterium began to appear at about the same time as Achromobacter and Arthrobacter species disappeared from the soil samples. Members of the genera Flavobacterium, Nocardia, and Pseudomonas were generally present throughout the test period. Unidentifiable yeasts began to invade the test plots during the last three months of the project.

The presence of Bacillus, Sarcina, and Streptomyces species is probably not significant and has no relationship to the disposal of hydrocarbons. These organisms may have invaded the plots at variable times due to dust contamination of the plots. The dust may have come from other areas.

Temperature appeared to have no effect upon the organisms present. Some of the highest counts were obtained during the winter months.

APPENDIX C

TABLE 1

STATISTICS OF MICROBIAL ANALYSIS

PERCENT TIMES ISOLATED FROM SAMPLES

| Genus | Plots A | B | C | Mean |
|---|---|---|---|---|
| Pseudomonas sp. | 88.8 | 72.2 | 94.4 | 85 |
| Flavobacterium sp. | 72.2 | 92.5 | 61.1 | 75 |
| Nocardia sp. | 77.7 | 62.9 | 77.7 | 72 |
| Corynebacterium sp. | 38.8 | 53.7 | 33.3 | 41 |
| Arthrobacter sp. | 31.4 | 25.9 | 14.8 | 24 |
| Unidentified yeasts | 22.2 | 14.8 | 27.7 | 21 |
| Saccharomyces sp. | 16.6 | 9.2 | 18.5 | 14 |
| Micrococcus sp. | 9.2 | 16.6 | 16.6 | 14 |
| Achromobacter sp. | 9.2 | 16.6 | 12.9 | 12 |
| Rhodotorula sp. | 5.5 | 9.2 | 3.7 | 6 |
| Sarcina sp. | 3.7 | 3.7 | 9.2 | 5 |
| Bacillus sp. | 3.7 | 1.8 | 3.7 | 3 |
| Streptomyces sp. | 1.8 | 3.7 | 3.7 | 3 |

APPENDIX C

MICROBIOLOGY CONSULTANT REPORT

Report of sampling of plots B-2 and C-2 with comparison counts on N.A. and 1% H.C. in nutrient agar media.

B-2 - 1% #6 Fuel oil
C-2 1% Paraffinate oil

| Nutrient Agar | Fuel |
|---|---|
| B-2<br>$31 \times 10^6$ cells/gm | B-2<br>$17 \times 10^6$ cells/gm |
| C-2<br>$5 \times 10^6$ cells/gm | C-2<br>$11 \times 10^5$ cells/gm |

Organisms - N.A.

B-2 Flavobacterium lutescens
Corynebacterium
Yeast IV
Corynebacterium

C-2 Yeast I
Yeast II
Yeast IV
Corynebacterium

Hydrocarbons

B-2 Only three isolated, checked for characteristics by streaking on N.A. plate

Corynebacterium sp. I
Corynebacterium sp. II
Yeast sp. IV

C-2 Only three org. isolated

Corynebacterium sp. IV
Pseudomonas sp. (unlike others)
Yeast sp. III

# APPENDIX D

## INFRARED STUDY OF OILS EXTRACTED FROM SOIL

### Method Summary

The infrared (IR) spectra of diluted oil samples were obtained on a Perkin-Elmer, Model 137, double-beamed spectrophotometer. Wavelength accuracy is ±0.03 microns. The oils were examined in matched NaCl absorption cells of 0.5 mm thickness.

The oil samples were prepared for IR scans by first dissolving a small portion of the oil in carbon tetrachloride ($CCl_4$). The sample was then centrifuged in a high-speed unit (5000 rpm) to remove very fine particles of soil entrained during the original extraction of the soil. The solvent was evaporated from the decanted solution under a nitrogen atmosphere at 250°F. Two solutions were prepared gravimetrically for scanning. The 2.0 to 9.0 micron (μ) region was scanned on a 4%w/v $CCl_4$ solution, and the 8.5μ to 15.0μ region was scanned on a 10%w/v carbon disulfide ($CS_2$) solution. Solvent absorption was cancelled by scanning the solvent simultaneously in the reference beam of the spectrophotometer.

### IR Band Assignments

The various structures from which the IR absorption bands arise are noted at the bottom of each of Figures 25-27. These assignments are well known but require some explanatory comments. The absorption near 2.9μ is assigned to OH groups other than those in organic acids. This absorption could also arise from NH groups; however, such materials are not present in waxy raffinate, yet the 2.9μ band is the most prominent in this material. The absorption intensity of this band in all of the samples is weak and appears to vary randomly. Since no special steps were taken to dry the oil samples or exclude small amounts of moisture during handling, the 2.9μ band may arise from small amounts of water. No further consideration will be given to this band.

There are four absorption bands that have been assigned to organic acids. The OH portion of the carboxyl group (COOH), when present as the dimer, exhibits a broad absorption on the long-wavelength side of the strong CH absorption band. This absorption is weak and difficult to see at low concentrations of organic acids.

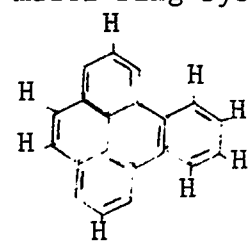
The sharp absorption band at 5.85μ has been attributed to the C=O of the acid group. This assignment has been verified by examination of a single oil sample in p-dioxane solution resulting in a shift of the C=O band to 5.75μ. The effect of polar solvent alone should produce a shift of the band to longer wavelength. The shift of the C=O band in

question to a shorter wavelength is indicative of dissociation of the acid dimer. Moreover, the actual shift to a shorter wavelength is less than would have been predicted by about the amount of reverse shift expected from the polar solvent. This prediction is based on Silverstein, R.M., and Bassler, G.C., Spectrometric Identification of Organic Compounds, Second Edition, John Wiley and Sons, Inc., New York, 1967. The assignment has been further verified by treating the oil sample with triethylamine in chloroform solution. This treatment resulted in a shift of the C=O band to about 6.3μ by conversion to the carboxylate ion, and the occurrence of a new band at 4.05μ indicative of the "ammonium band", also described by Silverstein and Bassler.

The absorption bands at 7.75μ and 10.6μ are assigned to the acid C=O stretching band and the OH bending of the dimer, respectively. At first glance, absorption will be noted in the 7.65 7.75μ range in all of the samples including the waxy raffinate. Absorption at 7.65μ is attributed to saturate groups; however, careful examination will reveal that, in those samples where the acid C=O absorption is strongest, this weak band is shifted to 7.75μ and becomes more pronounced.

The absorption band near 6.2μ is assigned to C=C groups in aromatic structures. This band can be used as a gross measure of aromatic content, but widely varying intensities among aromatic types limits its usefulness for quantitative measurements.

The absorption bands at 6.85μ and 7.25μ are assigned to $CH_2$ and $CH_3$ groups, respectively. It should be pointed out that these bands include such groups in both saturate molecules, per se, and in alkyl appendages on aromatic nuclei. The band at 13.88μ is the well known absorption arising from long paraffin chains; i.e., where four or more $CH_2$ groups are linked together in an uninterrupted sequence. Again, a five carbon sequence attached to an aromatic ring would also qualify.

The three strong absorption bands near 11.4μ, 12.2μ, and 13.2μ all arise from aromatic structures. The structures shown on the figures are intended only to illustrate the different configurations of the hydrogen atoms around the aromatic nucleus, as these absorption bands actually arise from the in-phase, out-of-plane vibrations of the hydrogen atoms. The position of the bands are actually dependent upon the number of hydrogen atoms that are adjacent to each other, and the aromatic nucleus can be a single or multi-ring system. Thus, in a polyaromatic ring system such as 

, where all hydrogen vacancies are occupied by R groups, all three configurations of hydrogen atoms are present.

## Results

The three different types of oils added to the soil test plots in the demonstration of oily waste disposal by the soil cultivation process, oil extracted from the soil at the start of the project, and oils extracted from the soil at the end of eight months (midway) and again at the end of the experiment (after 17 months), were examined by infrared spectroscopy. In between the 8-month and 17-month sampling periods, additional oils were added to the plots. The spectra of the oil samples where crude oil tank bottoms was added to the soil plots are designated as "A" plots and are shown in Figure 25. The "B" plots received bunker C oil (No. 6 fuel oil) and are shown in Figure 26. The "C" plots which were treated with waxy raffinate are shown in Figure 27. Different degrees of fertilization, which was a principal variable in the experiment, are noted on the figures.

### Oil Residue in Soil

The IR spectrum of the oil extracted from the soil at the beginning of this study is repeated in each figure for convenience, and has the gross character of a polyaromatic oil. Considerable evidence of saturate groups is observed at 6.85μ and 7.25μ together with a small amount of long chain paraffin groups at 13,88μ. The weak C=O band at 5.85μ indicates a small amount of organic acids. The other organic acid bands are not apparent, but treatment of this oil with triethylamine confirmed the presence of acid C=O structures.

### "A" Plots, Figure 25

The IR spectrum of the crude oil tank bottoms is typical of a saturate-aromatic oil mixture. The aromatic content is probably less than that in the oil extracted from the soil originally. This oil appears to contain simpler aromatic structures as evidenced by the differences in the 11-14μ region. As expected, there is no evidence of C=O structures.

The gross aromatic character of the oils extracted from all of the "A" plots are similar to that of the original oil extracted from the soil, indicating that the remaining oil in each case was more polyaromatic. There does not appear to be any significant effect of fertilizer upon the aromatic structures.

There is evidence of a small amount of long chain paraffin groups at 13.88μ, but the amount diminishes as the degree of fertilization is increased. After 17 months there is still some evidence of paraffin chains.

The most significant differences among the oils from the "A" plots are found in the organic acid content. After 17 months there is only a small amount of C=O structure in A-3, and the absorption for saturate groups at 6.85μ and 7.25μ are still quite strong. A-2 shows a large

increase in C=O band intensity and the other acid absorption bands are evident. There is a further small increase in organic acids in A-1, and the saturate groups at 6.85μ and 7.25μ decrease in both A-1 and A-2 as the organic acid groups increase. There is little difference in the results obtained on the samples from the "A" plots after eight months, except that the increase in organic acids was not as great with moderate fertilization as was observed for the sample after 17 months.

"B" Plots, Figure 26

The IR spectrum of the bunker C oil is typical of a polyaromatic oil and is quite similar to the oil extracted originally from the soil, except that there is less long chain paraffin content and an absence of organic acids.

After eight months' residence time, the aromatic characteristics of the oils from the "B" plots are quite similar and also similar to the original oil extracted from the soil. The results are similar to those in the "A" plots in that the long chain paraffin band is small and decreases with increased degree of fertilization. The organic acid content is evident but low in the spectrum of B-3; the other spectra show a progressive increase in plots B-2 and B-1 as the amount of fertilizer was increased. There is a concomitant decrease in the saturate groups at 6.85μ and 7.25μ with the increase in organic acids.

After 17 months, the IR spectra of the oils from the "B" plots indicate that something unique has occurred, since the organic acid content does not appear to increase in those plots where fertilizer was applied. There is also little change in the long chain paraffin groups in going from plots B-3 to B-1. An explanation for these results is offered in the body of this report.

The absorption at 9.65μ, attributed originally to aromatic materials, shows a broadening and an increase in intensity in the spectra of the original bunker C oil and also of plot B-2 after 17 months. This behavior is probably due to contamination by traces of dirt particles as silicas display absorption in this region of the IR spectrum.

"C" Plots, Figure 27

The IR spectrum of the waxy raffinate is typical of a nonaromatic oil. There is evidence of a very small amount of aromatics near 6.2μ. However, the principal absorption arises from the saturate groups at 6.85μ and 7.25μ and a large concentration of long paraffin chains at 13.88μ.

Oil extracted from each of the "C" plots is similar to that of the original oil in the soil. The spectra are typical of polyaromatic oils even though the added oil was principally paraffinic. This is not to suggest that the paraffin oils are converted to aromatics, but that

the paraffinic portion of the added oils was largely decomposed, even in the absence of fertilizer.

The amount of long chain paraffins remaining after 17 months in the unfertilized plot (C-3) was greater than that after eight months as evidenced by the 13.88μ band intensity. There was a higher concentration of long chain paraffins in both C-3 plots than in the oil present originally in the soil, indicating that some paraffin material survived the 17 months' residence in the soil. The amount of paraffinic material appeared to diminish in those plots where fertilizers were used.

The use of fertilizer enhanced the production of organic acids in proportion to the amount of fertilizer used as evidenced by the increased C=O band intensity at 5.85μ. The increase with moderate amounts of fertilizer was greater in the eight months sample. A significant decrease in saturate groups at 6.85μ and 7.25μ parallels the increase in organic acid C=O structures. The organic acid content was quite low in C-3 after 17 months but greater in C-3 after eight months. This difference inversely paralleled the change in long chain paraffin content as would be expected.

## INFRARED STUDY OF RAINFALL RUNOFF WATER

Infrared spectra of the oils recovered from samples of runoff water by $CCl_4$ extraction were obtained as conventional scans on the neat oils following the evaporation of the solvent.

Three nonvolatile oils (NVO) and two volatile oils (VO) recovered from samples of runoff water were selected for IR examination. These oils included NVO from plots A-1, B-1, and C-1, and VO from plots A-2 and C-1. The IR spectra of all of the oils were very similar and were identified as naphthenic acid concentrates by comparison with an IR spectrum of a naphthenic acids mixture obtained from Eastman Kodak Company. This identification has been confirmed from examination of the NVO from plots A-1 and C-1 by high-resolution mass spectiometry, which shows that both samples are very similar and that they consist of mixtures of naphthenic acids in the 200-300 molecular weight range. Small amounts of other saturated organic acids may be present.

The long chain paraffin based at 13.88 per is absent from the IR spectra in all but one of the oils (VO from plot C-1), and no significant amounts of aromatics are seen in any of the oil. Ultraviolet (UV) spectra of NVO from plots A-1 and C-1 (other oils were not examined by UV) are completely lacking in characteristic UV absorption, and thus tend to confirm the absence of significant amounts of aromatic structures.

# APPENDIX E

## OIL CONTENT IN SOIL SAMPLES

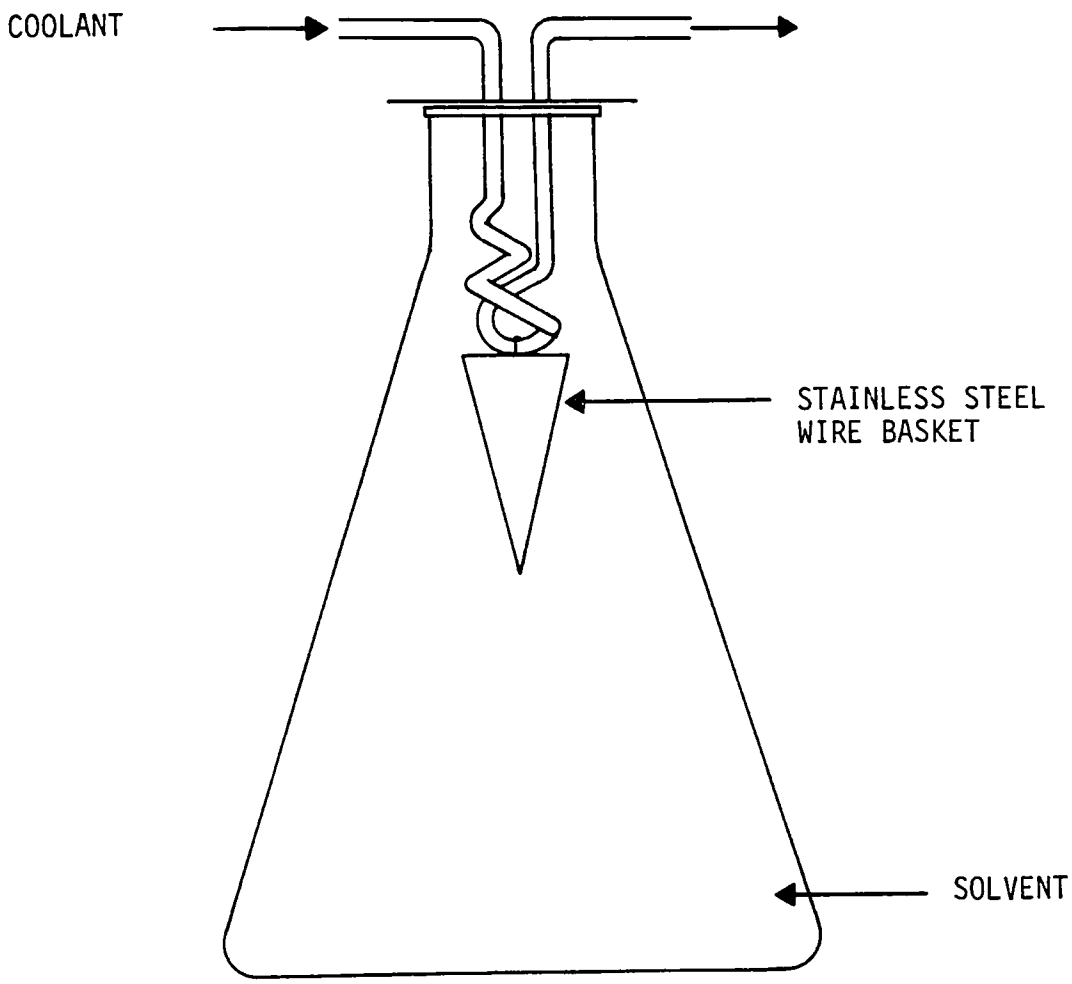
### Modified ASTM Method D-473, "Sedimentation in Fuel Oil by Extraction"

Modifications of ASTM method D-473[8] were made to adapt the method for determination of oily matter in soil. A change in the apparatus consisted of a stainless steel wire cone in place of the extraction thimble of D-473. A sketch of the modified apparatus is attached. For the test, a folded filter paper placed inside the cone held a weighed quantity of soil in a position beneath the condenser coil such that solvent condensate (condensed vapors) trickled through the soil and accomplished the extraction of oil from the soil. The solvent was carbon tetrachloride, C.P. grade, and the source of heat was an electrical heater (Ful-Kontrol, 750 watts).

The procedure included 1) placing a weighed soil sample inside the filter-paper lined, conical-wire basket, 2) drying the soil by placing the basket in an oven at 110°C for one hour, and 3) weighing the dry soil before extraction of the oil. The difference in weight before and after drying was considered to be water. The dried weighed soil was then placed in the extraction flask and extracted with carbon tetrachloride according to D-473 method procedure. After a period of two to three hours, and/or when the drops from the bottom of the wire basket appeared colorless, the heater was turned off and the sample allowed to cool. Then the condenser was removed and the carbon tetrachloride was evaporated, leaving the oily residue in the flask. Final evaporation was accomplished by introducing a stream of nitrogen gas into the heated oil-containing flask. Heat lamps were used for this final step. The flask containing the oil was weighed, then the oily residue was washed from the flask with carbon tetrachloride and a tare weight of the dry flask without the oil was obtained.

An alternate method was to oven-dry the soil sample after the extraction step and obtain the weight of the dry, oil-free soil.

For oily soil samples containing volatile components at the initial drying temperature of 110°C, the undried soil sample was weighed and extracted with carbon tetrachloride. The extracted soil was then oven dried and the difference in the initial weight and final weight was the total oil plus water. Oil was determined from the differences in the flask weights by the above described procedure and the water content was calculated by difference.




APPARATUS FOR EXTRACTION OF OIL IN SOIL



*U.S. GOVERNMENT PRINTING OFFICE:1973 514-151/137 1-3

| 1 Accession Number | 2 Subject Field & Group | SELECTED WATER RESOURCES ABSTRACTS<br>INPUT TRANSACTION FORM |
|---|---|---|
| W | 10A | |

5 Organization

SHELL OIL COMPANY, HOUSTON REFINERY
DEER PARK, TEXAS

6 Title

OILY WASTE DISPOSAL BY SOIL CULTIVATION PROCESS

10 Author(s)

Kincannon, C. Buford

16 Project Designation

EPA, Project No. 12050 EZG

21 Note

22 Citation

Environmental Protection Agency report number EPA-R2-72-110, December 1972.

23 Descriptors (Starred First)

*Oil Waste, *Sludge Treatment, *Soil Disposal Fields, *Soil Microbiology, *Sludge Disposal, Disposal, Soils Oil Industry, Oil, Water Pollution Sources, Industrial Waste, Wastes Bacteria, Decomposing Organic Matter, Biodegradation, Waste Disposal, Microorganisms, Aerobic Bacteria, Soil Bacteria Pseudomonas Fertilization, Drainage Effects, Fertilizers, Soil Treatment Nutrient Requirements, Ammonium Compounds, Nitrates, Phosphates, Potash, Ureas, Chromatography, Separation Techniques, Solvent Extraction Fertilizer.

25 Identifiers (Starred First)

Arthrobacter, Corynebacterium, Flavobacterium, Nocardia, Infrared Adsorption Oil Analyses

27 Abstract

Three oily materials were used in parallel experiments to demonstrate oily waste disposal by a soil cultivation process at prevailing climatic conditions. The 18-month experiments conducted with nine soil test plots at Deer Park, Texas, showed average oil decomposition rates of 0.5 lbs/ft$^3$ of soil per month without fertilizers and about 1.0 lb/ft$^3$/month when fertilized. Results of semi-monthly oil determinations for each plot are given. Major microbial species active in the soil were members of the genus Arthrobacter, Corynebacterium, Flavobacterium, Nocardia, and Pseudomonas. Predominant species in each soil test plot are reported on a monthly basis.

Differences in decomposition rate and microbial species due to hydrocarbon type as present in the three feedstocks, i.e., crude oil, bunker C fuel oil, and waxy raffinate oil were minimal. Infrared and gas chromatography examinations of oil extracted from fertilized and unfertilized soils showed differences in organic acid contents and boiling ranges.

Oil and fertilizer chemicals did not infiltrate vertically into the soil at the test location under prevailing conditions.

Rainfall runoff water contained 1) up to 100 ppm extractable oils found to be naphthenic acids and 2) up to 150 mg/l ammonia as N when the nitrogen nutrients were excessive in the soil.

Photographs show preparation of soil test plots, spreading of oil on the soil, and cultivation. Data are tabulated and shown graphically. (Kincannon-Shell)

| Abstractor | Institution |
|---|---|
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