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DISPOSAL OF OIL WASTES BY
MICROBIAL ASSIMILATION

H. C. Francke
F. E. Clark

UNION
CARBIDE

OAK RIDGE Y-12 PLANT
OAK RIDGE, TENNESSEE

*prepared for the U.S. ATOMIC ENERGY COMMISSION
under U.S. GOVERNMENT Contract W-7405 eng 26*

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Date Issued - May 16, 1974

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ABSTRACT

A biological assimilatory process for the disposal of plant oil waste products has been successfully demonstrated. The process involves mixing waste petroleum products into soil where naturally occurring microbial assimilation results in destruction of the oily wastes.

Disposal of waste oil and machine coolants was evaluated in laboratory tests and on six experimental field test plots comprising approximately one acre of land at the Oak Ridge Y-12 Plant. Approximately 15,000 gal (56.7 m³) of waste oil and 51,000 gal (193 m³) of machine coolant were spread on the cultivated and fertilized experimental plots over a four-month test period. Fertilizer and organic carbon losses on the test plots were minimal in rainwater surface runoff, in soil percolate water, and by evaporation. Disposal rates were greater than 1.5 lb of oil per ft³ of soil per month (24 kg/m³ per month) and 4.45 lb of coolant per ft³ of soil per month (71 kg/m³ per month).

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SUMMARY

Practical techniques for disposing of plant oil wastes utilizing natural soil microbial assimilatory processes have been demonstrated. Favorable results from initial experimental work indicated that oil wastes could be biologically decomposed under aerobic conditions when the oil was mixed within the top 6 in (0.15 m) of the surface soil. Intermittent cultivation was used to promote aerobic conditions in the top soil horizon, resulting in maximum microbial response. Combined oil/nitrate applications on a 0.088-acre (356-m²) plot showed an accelerated response.

During the period from May through August of 1973, regular weekly cultivations were possible except for two weeks when the soil was exceptionally wet. Fertilizer was distributed periodically on the waste oil and machine coolant plots at cumulative rates of 1600 to 1700 lb (726 to 772 kg) of nitrogen per acre ($4 \times 10^3 \text{ m}^2$). Loss of fertilizer or soluble organic carbon was found to be minimal in surface water runoff and in soil percolate waters found in 9-ft (2.7-m) test wells or in lysimeter soil/water percolate samples. Evaporation losses were 9 gal ($3.4 \times 10^{-2} \text{ m}^3$) of oil and less than 37 gal (0.14 m^3) of machine coolant in a 50-day test period.

The waste oil decomposition rate during the period from May 22 to September 6, 1973 was approximately 1 lb (0.45 kg) of carbon or 1.5 lb (0.7 kg) of waste oil per ft³ ($28 \times 10^{-3} \text{ m}^3$) of soil per month. The waste-oil cumulative application rate through September was approximately 1.15 gal ($4.35 \times 10^{-3} \text{ m}^3$) per ft² ($9 \times 10^{-2} \text{ m}^2$) of cultivated area. The machine coolant decomposition rate was approximately 0.34 lb (0.15 kg) of carbon or 4.45 lb (2.0 kg) of coolant per ft³ ($28 \times 10^{-3} \text{ m}^3$) of soil per month. The cumulative coolant application rate through September was 1.78 gal ($6.7 \times 10^{-3} \text{ m}^3$) per ft² ($9 \times 10^{-2} \text{ m}^2$).

INTRODUCTION

Biodegradation of oil is not new, but little practical application has been made of this characteristic. One of the first investigations into the utilization of microbial organisms for the disposal of hydrocarbons was made by Sohngen in 1906.⁽¹⁾ In 1913, he reported that gasoline, kerosene, paraffin oil, and paraffin wax could be oxidized to carbon dioxide, water, and traces of organic acids by commonly available microorganisms found in oil, ditch water, and compost.⁽²⁾ Stone, White, and Fenske⁽³⁾ found that oils containing a high percentage of paraffinic hydrocarbons were more readily assimilated than those containing aromatic compounds. Naphthenic fractions exhibited an intermediate reactivity.

Other researchers have indicated that most crude oils can be degraded biologically in the presence of mixed cultures of bacteria.⁽⁴⁾ Mixed cultures are preferred because there appears to be some selectivity in the ability of certain microbial species to attack various components of the oil. Although aerobic conditions appear to promote the most rapid degradation of oil, some investigators have oxidized mineral oil in the presence of nitrate which serves as a hydrogen acceptor under anaerobic conditions.⁽⁵⁾

Chemical emulsifying reagents improve the biodegradability of oils by exposing a greater hydrocarbon molecular surface to microbial enzymes and oxygen. Similarly, oil absorbed on chemically inert solids and fibers has been reported to be more susceptible to microbial oxidation.^(2 - 6)

As a result of the work of many investigators, it is evident that bacterial utilization of hydrocarbons can be induced in most common types of oils under optimum conditions. In fact, the oxidation of oil is similar in many respects to the oxidation of organic compounds, yielding such end products as carbon dioxide, water, organic acids, and some microbial biomass. More than a hundred species of bacteria, yeasts, and fungi have been found to oxidize one or more hydrocarbons. These microorganisms are widely distributed in oil field soils, sump waters, and coastal areas, particularly in localities subjected to frequent pollution by petroleum or refinery products.^(6 - 7) Thus, it appears that once a population of oil-oxidizing microorganisms become established in a soil-treatment plot, whether in an active or dormant state, they can be revitalized and reproduced upon further applications of oil. Hydrocarbons can be expected to be attacked wherever crude oil or its distillation products are in contact with water under conditions favorable for microbial growth. When thoroughly dispersed under aerobic conditions, as in soil soaked with oil, the hydrocarbons may be rapidly and quantitatively oxidized.⁽⁷⁾

A method for disposal of oily wastes by mixing with soil and utilizing soil microorganisms to decompose the oil at prevailing soil and climatic conditions has been demonstrated⁽⁴⁾ at the Shell Oil Company's Houston Refinery under partial sponsorship of the Water Quality Office of the Environmental Protection Agency. They reported an oil decomposition rate of approximately 1 lb per ft³ (16 kg/m³) of soil per month when commercial fertilizers were used to enrich the soil with nitrogen and phosphates. But, their tests also indicated that the oil and fertilizer compounds did not infiltrate vertically into the soil at the test location under prevailing climatic conditions. Rainfall runoff water sometimes contained up to 100 µg/ml extractable oils and ammonia as high as 150 µg/ml when nutrients were applied excessively to the soil. Differences in decomposition rate and microbial species for the hydrocarbon types tested were minimal.

Recognizing that appropriate methods, procedures, equipment, and operations depend on the individual situation, experimental soil-disposal tests have been conducted in the laboratory and on field plots of the Oak Ridge Y-12 Plant.^(a) Favorable responses from these experimental tests indicated that oil wastes could be biologically decomposed aerobically when the top six inches (0.15 m) of the soil was cultivated intermittently. Cultivation was necessary to promote aerobic conditions for maximum microbial response. Periodic cultivation may be limited, however, by climatic conditions, particularly during months of heavy rainfall.

Due to the generally favorable response achieved in small-scale experimental disposal of oil wastes, field experimental plots were constructed and are currently receiving applications of waste oil and coolant. This report covers progress being made in spreading the oil and coolant wastes, cultivation of the soil, and includes effluent and soil analyses.

(a) Operated by the Union Carbide Corporation's Nuclear Division for the United States Atomic Energy Commission.

WASTE OIL AND COOLANT DISPOSAL

EXPERIMENTAL WORK

Current Oil Disposal Practices

Current oil disposal practices involve plant-wide collection of waste oil and oil-based coolants. Part of the waste oils are purified using a molecular sieve filtration unit; some are buried in steel drums in solid waste disposal trenches. (8)

Laboratory and Small-Scale Field Experiments

Initially, incineration was considered to be a possible method for the disposal of oily wastes. But, because of stack emission standards, economic considerations for plant investment in scrubbers and precipitators to remove toxic compounds have made this method seem less attractive. Anticipated high maintenance costs and probably equipment downtime were additional factors that led to the investigation of other disposal techniques. Data are presented in Table 1 showing the impurities found, expressed in pounds (lb) of metallic oxides, resulting from the incineration of 10,000 gal (38 m³) of waste crankcase oil from nine cities throughout the United States. As can be seen, these oils contained high levels of lead, calcium, and phosphorus.

Presented in Appendix A (Table A-1) are analytical data on impurities found in waste oils collected at the Oak Ridge Y-12 Plant. These analyses are not on the ash, but on raw or carbonized waste oil. These data indicate that the oils contained high levels of calcium, iron, sodium, silicon, phosphorus, chlorine, zinc, and lead.

A common method of analyzing oil for inorganic impurities is to burn and analyze the residue, but this method has the disadvantage of losing elements which form volatile products during the burning process. Wet digestion employing conventional nitric and perchloric acids was tried, but the technique was found to be both uneconomical and inaccurate. Also, heavy contamination, particularly by borosilicate glass, was found in the final solution. A method was finally developed which was reasonable in cost and still provided the desired accuracy. A known amount of oil was dried on a pure carbon electrode and excited by a high-frequency spark. The resulting mass spectra were recorded on a photographic plate and compared to standards in a densitometer. This method of analysis has been used as a basis for experimental evaluation of impurities in oils in some of the present work (Table A-1).

Table 1
IMPURITY LEVELS FOUND IN WASTE CRANKCASE OIL AFTER INCINERATION

Impurity	Range of Products ⁽¹⁾	
	(lb)	(kg)
Zinc	32 - 58	15 - 26
Copper	0.9 - 1.6	0.4 - 0.7
Aluminum	2.6 - 6.3	1.2 - 2.9
Barium	9.3 - 57	4.2 - 26
Calcium	120 - 220	54 - 100
Nickel	0.2 - 2.4	0.1 - 1.1
Chromium	1.2 - 4.8	0.5 - 2.2
Iron	17 - 42	7.7 - 19
Silicon	13 - 64	5.9 - 29
Lead	400 - 720	181 - 327
Tin	0.6 - 1.3	0.3 - 0.6
Phosphorus	173 - 264	78 - 120
Boron	2.8 - 5.9	1.3 - 2.7
Magnesium	10 - 61	4.5 - 28

(1) As oxides/10,000 gal (38 m³) of waste crankcase oil.
Source: EPA, based on tests conducted at nine US sites by members of APR.

Table 2 indicates the degree of oil degradation with time for two test plots. These data are inconclusive due to the difficulty in obtaining a truly representative sampling of the test plots. Actual biodegradability of the oil, however, appears to be in the range of 25 to 50 wt % for a period of seven months. During this period, generally unfavorable climatic conditions, characterized by low temperatures and above-average precipitation, prevailed. This set of conditions had an adverse effect on microbial activity.

A preliminary bacterial degradation experiment was also performed in the laboratory using a polyethylene bottle equipped with a tubing inlet and outlet. A mixture of 7 kg of dry soil, 0.7 kg of used vacuum pump oil, and 0.5 kg of water was placed in the bottle. The bottle, sealed and 15 cm³/min (2.7×10^{-7} m³/sec) of instrument air, was passed from the bottom of the bottle, through the soil, and vented through a bubbler. Carbon dioxide was exhausted through the vent tube and measured. The weight of carbon lost from the mixture per day was calculated. Figure 1 shows the cumulative carbon loss for a 90-day period.

The machine coolant used in the Y-12 Plant is an emulsion of about 80% water and 20% oil. The oil/water emulsion can be separated by adding chemical salts. Since soil is a well-known and widely utilized chromatographic and ion-exchange medium, a 2-in (0.051-m) column of soil was also utilized to disperse an emulsified machine coolant. About 1200 ml (1.2×10^{-3} m³) of coolant (20% coolant oil and 80% water) was poured on top of the soil column. All of the oil was retained in the soil column; the liquid leaving the column was clear. This experiment was readily reproducible in the laboratory.

Figure 1. CUMULATIVE CARBON LOSS (AS CO₂) AS A FUNCTION OF TIME.

To further measure the biodegradability rates, two large oil-impregnated test plot experiments were initiated in August 1972. Each plot, consisting of tilled ground, was 10 ft wide (3.0 m), 24 ft long (7.3 m), and 1 ft deep (0.3 m), and subdivided into four subplots by earth dikes. Each subplot was about 6 ft wide (1.8 m), 10 ft long (3.0 m), and 1 ft deep (0.3 m). One of the test plots was made up of a reasonably tillable and friable loam-type soil containing some shale; the second plot was composed of heavy clay. Figure 2 gives a view of the loam/shale type of soil after a heavy rain. Heavy concentrations of used crankcase oil show as dark areas in the bottom of the middle subplot. The subplot on the extreme left

Table 2
DEGREE OF OIL BIODEGRADABILITY WITH TIME

Plot 1											
Subplot Numbers	1	1	1	1	4	4	4				
Date Sampled	8-27-72	9-1-72	11-7-72	2-1-73	9-22-72	11-7-72	2-1-73				
Type Oil Added	None	Mixed Coolant	Mixed Coolant	Mixed Coolant	Vacuum Pump	Vacuum Pump	Vacuum Pump				
Percent Oil	< 0.01	1.00	0.69	1.00	6.90	4.80	4.90				
Percent Carbon	0.17	1.93	1.41	1.23	6.93	5.29	4.47				
Plot 2											
Subplot Numbers	1	1	1	1	2	2	4	4	4	4	4
Date Sampled	8-25-72	9-1-72	11-7-72	2-1-73	11-7-72	2-1-73	8-27-72	9-1-72	9-22-72	11-7-72	2-1-73
Type Oil Added	None	Mixed Coolant	Mixed Coolant	Mixed Coolant	Crank- case	Crank- case	None	Vacuum Pump	Vacuum Pump	Vacuum Pump	Vacuum Pump
Percent Oil	< 0.10	2.30	1.60	1.40	6.50	6.20	< 0.10	8.0	8.70	7.40	2.70
Percent Carbon	0.81	2.13	2.41	2.20	6.71	6.46	0.96	7.17	7.18	7.41	6.31

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Figure 2. LOAM/SHALE-TYPE SOIL SUBPLOTS AFTER OIL APPLICATIONS.

had about 600 gal (2.3 m^3) of mixed machine coolant added and the soil had been tilled several times before it was settled by the rain on the day before this photograph was taken. The crankcase oil and vacuum pump oil-impregnated soils were more friable than the soils in the adjacent control subplots which received no oil, and cultivated similar to soils containing a large quantity of humus.

Combined Oil/Nitrate Application Experiment

Since spent oils are essentially carbonaceous materials, a field experiment was designed for alternate applications of oil and waste nitrate solutions. The experiment was designed to serve a twofold purpose of disposing of waste oil as well as nitrate waste solutions which could possibly accelerate microbial response.

A circular test plot, comprising 0.088 acre (356 m^2) of barren clay soil, was constructed for an experimental oil/nitrate disposal site. Pulverized limestone was spread at the rate of one ton (910 kg) per acre ($4 \times 10^3 \text{ m}^2$) and thoroughly mixed in the upper 12 in (0.3 m) of the tilled clay surface layer. Limestone was added because of the naturally occurring clay soil which consisted largely of decomposed shale, and exhibited an initial pH of 3.83. The spectrochemical analysis results are reported in Appendix A, Table A-2. The subsequent

limestone-buffering action was sufficient to raise the soil pH to 5.43. The initial carbon content of the natural clay was 0.445 wt %; uranium background in the clay was 1 $\mu\text{g/g}$. Spectrographic analyses indicate that the clay was basically an aluminum silicate with minor quantities of boron, calcium, iron, magnesium, manganese, potassium, sodium, and titanium. A field drain tile system was installed under the test plot at a depth of three feet (0.9 m) with the fill being firmly compacted to match the adjacent soil. This system provided a satisfactory method for sampling the percolate water issuing from the experimental plot. Spectrochemical analyses of the percolate water prior to the application of oil or nitrate are presented in Appendix A, Table A-3. A period of relatively dry weather preceded the initial application, permitting the site to be readily cultivated. Straw was spread over the surface to furnish a protective cover. A single, full-rotation sprinkler was installed in the center of the plot to facilitate spray application of both oil and nitrate solutions, as seen in Figure 3.

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Figure 3. CIRCULAR TEST PLOT SHOWING SITE PREPARATION AND OPERATION OF SPRINKLER FOR OIL/NITRATE APPLICATIONS.

Small experimental quantities of oil and nitrate solutions were applied on October 3 and 6; however, a bulk of the application was made on October 10 and 11 (Table 3). A total of 1070 gal (4 m³) of lubricating oil, cutting oil, vacuum pump oil, and machine coolant were sprayed on the plot. Alternate applications of calcium nitrate solution amounted to 323 gal

Table 3
SUMMARY OF OIL/NITRATE SPRAY APPLICATIONS ON EXPERIMENTAL PLOT 1

Type Application ⁽¹⁾	Date Applied	Volume		Time (m n)	Rate		Oil		Quantity			
		(gal)	(m ³)		(gpm)	(m ³ /s)	(gal/acre)	(m ³ /m)	NO ₃ ⁻		NO ₃ ⁻	
									(lb)	(kg)	(lb/acre)	(kg/m ²)
Lube Oil ⁽²⁾	10-3-72	70	0.26	22	3.2	2×10^{-4}	795	7.4×10^{-4}				
Ca(NO ₃) ₂ ⁽³⁾	10-3-72	35	0.13	10	3.5	2×10^{-4}			3.4	1.5	39	3.7×10^{-4}
Ca(NO ₃) ₂	10-6-72	18	0.07	3.5	3.4	2×10^{-4}			1.7	0.8	19	1.9×10^{-4}
Cutting Oil, Building 9201-1	10-10-72	350	1.3	58	6.0	4×10^{-4}	3,977	3.7×10^{-3}				
Vacuum Pump Oil, Building 9202	10-10-72	250	0.9	42	6.0	4×10^{-4}	2,841	2.6×10^{-3}				
Ca(NO ₃) ₂	10-10-72	120	0.45	20	6.0	4×10^{-4}			11.5	5.2	131	1.2×10^{-3}
Vacuum Pump Oil, Building 9202	10-11-72	100	0.38	20	5.0	3×10^{-5}	1,136	1×10^{-3}				
Coolant, Building 9212	10-11-72	300	1.1	60	5.0	3×10^{-4}	3,409	3×10^{-3}				
Ca(NO ₃) ₂	10-11-72	150	0.57	25	6.0	4×10^{-4}			14.4	6.5	163	1.6×10^{-3}
Total Oil		1070	4.0				13,159	1.1×10^{-2}				
Total Ca(NO ₃) ₂		323	1.2						31.0	14.0	352	3.4×10^{-3}

(1) Plot area 0.088 acre (356 m²).

(2) Oil density 0.77 pound per gallon (92 kg/m³).

(3) Calcium nitrate solution contained 0.96 pound per gallon (11 kg/m³) NO₃⁻.

(1.2 m³), equivalent to 31 lb (14 kg) as the nitrate. Oil application was equivalent to 12,159 gal (46 m³) per acre (4050 m²) and nitrate was equal to 352 lb (160 kg) per acre (4050 m²). Spectrochemical analyses of the calcium nitrate solution are presented in Appendix A, Table A-4.

From October 12 through October 19, 1972, heavy precipitation occurred with cumulative rainfall totaling 5.08 in (0.13 m) during this week (Appendix A, Table A-5). It was evident from the data collected on percolate water that oil and nitrate losses were relatively high during the first week, totaling 128.7 lb (58 kg) of oil and 13.03 lb (5.9 kg) of nitrate. In terms of the total amount of oil and nitrate applied, the first week weight losses were 1.56 and 42.03%, respectively (Table 4). Cumulative losses of oil and nitrate for a five-week monitoring period are reported in Table 4, which indicate a significantly diminishing weight loss for each successive week as biodegradation proceeded.

Table 4
OIL AND NITRATE LOSSES IN SUCCESSIVE WEEKS AFTER APPLICATION

Elapsed Time (weeks)	Oil Content		Weight Loss (%)	Nitrate Content		Weight Loss (%)
	(lb/wk)	(kg/wk)		(lb/wk)	(kg/wk)	
1	128.70	58.4	1.56	13.030	5.9	42.03
2	4.72	2.1	0.06	3.540	1.6	11.42
3	3.87	1.8	0.05	0.521	0.2	1.68
4	3.00	1.4	0.04	0.339	0.1	1.09
5(1)	1.14	0.5	0.01	0.095	0.04	0.31
Cumulative						
Total	141.33	64.1	1.72	17.525	7.9	56.53

(1) Five days only.

Chemical and spectrographic analyses of a soil sample taken from the top 6-in (0.15-m) surface layer of the experimental plot three weeks after application of oil and nitrate are summarized in Tables 5 and 6. A significant increase was noted in the carbon content in Table 5, as expected. Approximately 2.3 wt % oil was extracted from the top 6-in (0.15-m) soil layer, indicating incomplete decomposition. Initial concentration of oil in the soil surface layer was approximately 7.4 wt %. This concentration indicated biodegradation of approximately 70% in the first three weeks. The amount of residual nitrate in the soil was 118 µg/g and represented a gain over the original 31 µg/g. No change was indicated for the ammonium ion. Organic nitrogen, an indicator of assimilatory microbial conversion of nitrate to amines and proteins, was present in a significant amount (0.052%), also shown in Table 5.

In the spectrographic soil analysis, Table 6, slight gains were indicated for calcium, magnesium, and manganese, with minor reductions in potassium and sodium. Subsequent samples of the percolate water on December 4 and 18 indicated essentially no further loss of oil or nitrate.

Data obtained from the experimental plot indicated that biological degradation, once initiated, appeared to proceed rapidly after a three to four-day incubation period in warm

Table 5
CHEMICAL ANALYSIS OF COMPOSITE SOIL
SAMPLE THREE WEEKS AFTER SPRAY
APPLICATION OF OIL AND
NITRATE SOLUTION

	Concentration ($\mu\text{g/g}$)		Content (wt %)
NO_3^-	118.0	C	3.09
NH_3	52.0	H	1.10
		N	0.052
		Oil	2.30
pH	5.43	U	0.0003
Density			
		(g/ml)	(kg/m^3)
Absolute Soil	2.0117		2011
Soil Pour	0.90		900
Soil Pack	1.23		1230

weather (20 to 22°C soil temperature), but slowed during cold, rainy weather (5 to 15°C soil temperature). pH of the percolate water ranged between 6.55 and 8.06 and, in this range, contained essentially no soluble uranium (0.01 to 0.08 $\mu\text{g/g}$).

Because of the abnormally heavy rainfall throughout the period of observation and a resulting lack of cultivation, there was moisture saturation on the plot which may have resulted in oxygen depletion and anaerobic conditions.

Description of Field Experiment

Engineering drawings were prepared for grading and construction of a large-scale field disposal site (Figure 4), and six plots, 12 ft (3.66 m) wide and approximately 550 to 600 (167 to 183 m) ft in length were constructed. Experiments were initiated and continued throughout the summer of 1973, using the six plots. Two 550-ft (167-m) plots (Plots 1 and 2), with 50-ft (15-m) control strips, were used for disposal of waste oil. Four 600-ft (183-m) plots (Plots 3 through 6), were used for machine coolant disposal. The disposal site is relatively level, as seen in the photographic view (Figure 5), has satisfactory natural drainage, and is located approximately 100 yd (91 m) north of a sanitary landfill site. Initial preparation of the site included the spreading and working of 1.3 tons (1.2 Mg) of agricultural-grade limestone into each plot. The limestone serves to buffer the soil acidity. Additional applications of limestone will be made as needed on an annual or semiannual basis. The pH of the soil in the plots was monitored on a regular basis and has remained at near 7. Agricultural fertilizer and neutralized nitrate waste effluents were applied to each plot to provide a cumulative application of approximately 1000 lb (454 kg) per plot of nitrogen with lesser quantities of phosphorus and potassium to meet the microbial nutrient requirements.

Table 6
SPECTROGRAPHIC ANALYSIS OF COMPOSITE SOIL
SAMPLE THREE WEEKS AFTER APPLICATION
OF OIL AND NITRATE SOLUTION
(Sampled on 11/2/72)

Element	Concentration (%)	Element	Concentration (%)
Ag	< 0.005	Mo	< 0.002
Al	20.0	Na	0.04
Au	< 0.02	Nb	< 0.02
B	0.04	Ni	0.01
Ba	0.01	P	< 1.0
Be	< 0.001	Pb	< 0.01
Bi	< 0.01	Pd	< 0.002
Ca	0.3	Pt	< 0.02
Cd	< 0.04	Rh	< 0.15
Co	< 0.005	Sb	< 0.04
Cr	< 0.01	Si	> 20.0
Cs	< 0.6	Sn	< 0.005
Cu	< 0.005	Ta	< 0.15
Fe	5.0	Th	< 0.04
Hf	< 0.02	Ti	0.6
K	0.6	V	< 0.005
Li	< 0.02	W	< 0.08
Mg	5.0	Zn	< 0.08
Mn	0.6	Zr	0.02

Figure 4. OIL DISPOSAL PLAN.

Figure 5. OIL DISPOSAL SITE.

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Waste oil and coolant are stored separately at the point of collection and each is spread on specified plots as evenly as practical using a 5,000-gal (19-m^3) mobile tanker equipped with a spreader boom. A photograph of the tanker in operation is presented in Figure 6. The quarterly application rate amounted to more than 0.5 gal ($2 \times 10^{-3}\text{ m}^3$) of oil per

Figure 6. FIVE-THOUSAND-GALLON TANKER IN OPERATION.

151482

ft^2 ($9 \times 10^{-2} \text{ m}^2$). Once the allocated quota of oil was spread on a plot, no additional oil was applied until biodegradation was observed to be well advanced. The application rate corresponded to that used by the Shell Oil Company in their experimental project for the Environmental Protection Agency,⁽⁴⁾ completed during 1972, but was less than previously used on small cultivated test plots. One-half gallon ($2 \times 10^{-3} \text{ m}^3$) of oil per ft^2 ($9 \times 10^{-2} \text{ m}^2$) per quarter was equivalent to an annual disposal rate of 14,400 gal (54.5 m^3) per year per 550-ft (167-m) strip, or 87,000 gal (329 m^3) per acre ($4 \times 10^3 \text{ m}^2$) per year. Soil cultivation was scheduled weekly, depending on climatic conditions and usually followed directly after each application of oil. A photograph of the tractor-pulled, disc cultivator is given in Figure 7.

Application of Oil and Coolant

The first application of waste oil was made on May 16, 1973. In this operation, a total of 33,280 lb (15 Mg) [4493 gal (17 m^3)] of waste oil was spread on Plots 1 and 2. This application was equivalent to 0.34 gal ($1.29 \times 10^{-3} \text{ m}^3$) of waste oil per ft^2 ($9 \times 10^{-2} \text{ m}^2$) for the area covered. Plots 1 and 2 received additional applications of 18,120 lb (8.2 Mg) [2446 gal (9.2 m^3)] on May 21, 20,440 lb (9.3 Mg) [2,760 gal (10.4 m^3)] on July 11, and 39,140 lb (18 Mg) [5284 gal (20 m^3)] on September 11. Total applications of waste oil on Plots 1 and 2 through September 11 (Table 7) amounted to 110,980 lb (50

Figure 7. TRACTOR-TOWED DISC CULTIVATOR.

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Mg) [14,983 gal (56.7 m³)]. This amount is equivalent to a total four-month application rate of 8.4 lb (3.8 kg) or 1.135 gal (4.3 x 10⁻³ m³) per ft² (9 x 10⁻² m²) for cultivated Plots 1 and 2. The four-month application rate, if allowances were made for adverse climatic conditions during the winter months, was projected to 2.0 gal (7.6 x 10⁻³ m³) per ft² (9 x 10⁻² m²) per year or 87,000 gal (329 m³) per acre (4 x 10³ m²) per year.

A total of 418,470 lb (190 Mg) [51,208 gal (194 m³)] of machine coolant was applied to Plots 3 through 6 through September 21 (Table 7). This amount represents a four-month coolant application rate of 14.53 lb (6.6 kg) [1.78 gal (6.7 x 10⁻³ m³)] per ft² (9 x 10⁻² m²). If projected during favorable weather on an annual basis of eight months, the rate would be 3.56 gal (13.5 x 10⁻³ m³) per ft² (9 x 10⁻² m²), or 155,000 gal (587 m³) per acre (4 x 10³ m²) per year. It should be noted that significantly higher application rates can be tolerated with coolant since its carbon content ranges from 3.3 to 12.4% versus 73.1 to 83.01% for waste oils (Appendix A, Tables A-6 and A-7).

Cultivation

Although rainfall was excessive in May, June, and July [19.31 in, (0.49 m)], cultivation of the soil was possible in all weekly periods except two. These two weekly periods had

Table 7
SCHEDULE OF OIL AND COOLANT APPLICATIONS

Date (1973)	Waste Oils				Coolant			
	(lb)	(Mg)	(gal)	(m ³)	(lb)	(Mg)	(gal)	(m ³)
May 16	33,280	15	4,493	17	-	-	-	-
May 18	-	-	-	-	32,720	15	4,014	15
May 21	18,120	8	2,446	9	-	-	-	-
June 5	-	-	-	-	28,460	13	3,500	13
June 15	-	-	-	-	28,400	13	3,493	13
June 19	-	-	-	-	6,960	3	856	3
June 20	-	-	-	-	43,200	20	5,314	20
July 9	-	-	-	-	24,350	11	2,995	11
July 11	20,440	9	2,760	10	-	-	-	-
July 13	-	-	-	-	43,360	20	5,333	20
July 30	-	-	-	-	32,640	15	4,015	15
August 8	-	-	-	-	16,000	7	1,968	7
August 8	-	-	-	-	28,860 ⁽¹⁾	13	3,492	13
August 10	-	-	-	-	2,080	1	256	1
August 19	-	-	-	-	45,270	21	5,568	21
September 1	-	-	-	-	36,820 ⁽¹⁾	17	4,456	17
September 10	-	-	-	-	21,320 ⁽¹⁾	10	2,558	10
September 11	39,140 ⁽²⁾	18	5,284	20	-	-	-	-
September 21	-	-	-	-	28,020 ⁽¹⁾	13	3,390	13
TOTAL	110,980	50	14,983	57	418,470	190	51,208	194

(1) Mixture of coolant and mop waters - 3.3% carbon content.

(2) Floating oil recovered from retention pond - 83% carbon content.

3.26 and 4.60 in (0.08 and 0.12 m) of rainfall. During the relatively dry months of August and September, no such problem existed. Because of the high water content in the coolant (which rapidly evaporated during the hot, dry weather), cultivations were made during application and on the following day. Heavy applications of waste oil on Plots 1 and 2 required at least two days before the soil could be cultivated. Continued cultivation tends to produce a subsurface hard pan which appears to retard oil infiltration into the subsoil.

Application of Fertilizers

Commercial-grade fertilizers were used except for one test. Schedules for fertilizer application for Plots 1 and 2 and Plots 3 through 6 are listed in Tables 8 and 9, respectively. During the four-month period, the two waste-oil plots (Plots 1 and 2) received a total application of 484 lb (220 kg) of elemental nitrogen and 105 lb (48 kg) each of potassium and phosphorus. During the same period, the four machine-coolant plots (Plots 3 through 6) received 565 lb (256 kg) of nitrogen and 145 lb (66 kg) each of potassium and phosphorus. A composite soil sample collected on September 4 contained 0.0964% total nitrogen, which calculates to be 491 lb (223 kg) of nitrogen on experimental Plots 1 and 2. This calculation indicates that loss of nitrogen to the environment appears to have been minimal. Analysis included organic nitrogen, nitrate, ammonia, and nitrites.

An effective method for introducing moisture into the soil during extremely dry periods was the use of a water solution of calcium nitrate (containing approximately 0.1% nitrate

Table 8
APPLICATION OF FERTILIZER TO PLOTS 1 AND 2

Date (1973)	Fertilizer Type	Fertilizer		Nitrogen		Potassium		Phosphate	
		(lb)	(kg)	(lb N)	(kg)	(lb K ₂ O)	(kg)	(lb P ₂ O ₅)	(kg)
May 13	15-15-15	100	45	15	7	15	7	15	7
June 8	15-15-15	200	90	30	14	30	14	30	14
June 22	NH ₄ NO ₃ ⁽¹⁾	400	180	136	62	-	-	-	-
July 6	NH ₄ NO ₃	300	136	102	46	-	-	-	-
July 20	20-10-10	400	180	80	36	40	18	40	18
August 6	20-10-10	200	90	40	18	20	9	20	9
September 10	NO ₃ ⁽²⁾	360	163	81	37	-	-	-	-
Total Fertilizer Applied in Four Months				484 ⁽³⁾	220	105	48	105	48
Pounds per Acre				1597		347		347	
Kg per m ²					0.18		0.04		0.04

(1) Ammonium nitrate fertilizer - 34% nitrogen.

(2) Neutralized nitrate effluent.

(3) Total nitrogen in Plots 1 and 2, based on September 4 composite soil analysis, was 491 pounds (223 kg).

Table 9
APPLICATIONS OF FERTILIZER TO PLOTS 3 THROUGH 6

Date (1973)	Fertilizer Type	Fertilizer		Nitrogen		Potassium		Phosphate	
		(lb)	(kg)	(lb N)	(kg)	(lb K ₂ O)	(kg)	(lb P ₂ O ₅)	(kg)
May 13	15-15-15	100 ⁽¹⁾	45	15	7	15	7	15	7
June 8	15-15-15	100 ⁽¹⁾	45	15	7	15	7	15	7
June 19	15-15-15	100 ⁽²⁾	45	15	7	15	7	15	7
June 22	NH ₄ NO ₃ ⁽³⁾	200	90	68	31	-	-	-	-
July 6	NH ₄ NO ₃	400	180	136	62	-	-	-	-
July 20	20-10-10	800	360	160	73	80	36	80	36
August 6	20-10-10	200	90	40	18	20	9	20	9
August 10	NO ₃ ⁽⁴⁾	273	124	62	28	-	-	-	-
September 10	NO ₃	120	54	54	25	-	-	-	-
Total Fertilizer Applied in Four Months				565	256	145	66	145	66
Pounds per Acre				1709		439		439	
Kg per m ²					0.19		0.05		0.05

(1) Fertilizer applied to Plots 3 and 4 only.

(2) Fertilizer applied to Plots 5 and 6 only.

(3) Ammonium nitrate fertilizer - 34% nitrogen.

(4) Neutralized nitrate effluent.

ion), which was used for only one application. The oil transport tanker was used to apply the nitrate solution. Use of nitrate in solution has the further advantage of immediate utilization by organisms in the soil which appears to fix the nitrogen in an organic form. Subsequent surface runoff and infiltration of nitrates is, therefore, less during periods of rainfall than that experienced with dry, granular fertilizers.

Effluent Sampling and Analysis

Surface runoff water was sampled during or immediately after periods of rainfall when estimated effluent flows ranged from 0.1 to 20 gpm (0.006 to $1.3 \times 10^{-3} \text{ m}^3/\text{s}$). The total volume of water can only be approximated because runoff occurred only during or after a rainfall. Maximum loss of nitrate and organic carbon occurred during a rainfall following fresh applications of oil or coolant. During the four-month test period, total organic carbon (TOC) and nitrate analyses of surface waters draining from the six oil plots showed considerable variations, 10 to 983 $\mu\text{g}/\text{ml}$ for carbon and 6 to 738 $\mu\text{g}/\text{ml}$ for the nitrate ion (Appendix A, Tables A-8 through A-12). These losses were not significant amounts when compared with the total quantity of oil and machine coolant applied to the plots.

Analysis of percolate water from the east and west streams which drain the general watershed areas in proximity to the oil plots has shown TOC values ranging from 14 to 38 $\mu\text{g}/\text{ml}$ (Appendix A, Tables A-8 through A-12). Nitrate samples contained 3 to 38 $\mu\text{g}/\text{ml}$. These values approximate the background levels for these small streams.

Ten 9-foot (2.7-m)-deep test wells for sampling percolate water were drilled along the south and west roadways that parallel Plot 6 and follow the natural slope of the topography of the existing plots. The ten wells intercepted percolate ground waters flowing out of the test area. Analyses following rainfall on September 14 and 17 are presented in Table 10 and do not show any significant loss of nitrate or organic carbon.

Table 10
PERCOLATE WATER ANALYSES OF
OIL-PLOT TEST WELLS

Test Well Number (1)	pH	NO_3^- ($\mu\text{g}/\text{ml}$)	Total Carbon ($\mu\text{g}/\text{ml}$)	Total Organic Carbon ($\mu\text{g}/\text{ml}$)
1	7.05	0.6	76	15
2	7.47	7.2	142	13
3	7.67	14.1	73	15
4	7.79	11.3	40	12
5	7.19	1.7	155	19
6	7.14	25.6	151	33
7	7.53	31.8	78	9
8	7.55	7.9	86	7
9	7.63	< 0.2	62	6
10	7.47	0.6	77	11

(1) Test Wells 3 and 4 were sampled on 9-14-73; all other wells were sampled on 9-17-73.

Soil Water Percolate Analysis

To assess the quality of water percolating beneath the oil disposal area, tube lysimeters were installed in the test plots at a depth of 60 cm. Two lysimeters were placed in a control section, three were placed in the waste oil pits, and three were placed in the waste coolant pits. Table 11 gives a summary of the nitrate and organic carbon content of the soil water percolate from June 6 through August 1. Tables A-13 and A-14, Appendix A, present the complete data for information purposes. Graphs of the oil and nitrogen losses are presented in Figures 8 and 9.

Values obtained from the lysimeter sampling system exhibit greater variability than have been experienced with similar installa-

tions in virgin soil. Variability of the fill material comprising the disposal area and lack of a well-developed soil structure allowing channelization of water may account for the observed variance. Cultivation activities also could have disturbed the lysimeter installations such that surface water moved freely down the outside surface of the lysimeter tube.

Table 11
ESTIMATED LOSSES OF NITRATE AND ORGANIC CARBON VIA SOIL WATER
PERCOLATION BELOW 75 CENTIMETERS

	Control Plots		Oil Plots		Machine Coolant Plots	
	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum
Mean Concentration ⁽¹⁾						
Nitrate ($\mu\text{g/ml}$)	85	1.37	14	1.02	43	0.9
Organic Carbon ($\mu\text{g/ml}$)	7.1	-	14.6	-	91	17.3
Water Flux						
(10^6 lb)	1.208	-	1.208	-	1.208	-
(Mg)	548	-	548	-	548	-
Loss of Nitrate						
(lb/plot)	23.2	0.35	3.8	0.27	11.7	0.21
(kg/plot)	10	0.16	1.7	0.12	5.3	0.10
Loss of Organic Carbon						
(lb/plot)	8.57	-	17.46	-	110.61	20.95
(kg/plot)	3.9	-	7.9	-	50.2	9.5

(1) Concentrations are averaged over all dates. Tubes are averaged over all dates, deleting values not considered representative.

Figure 8. TOTAL ORGANIC CARBON LOSSES IN PERCOLATE WATER.

Figure 9. NITRATE LOSSES FROM OIL AND COOLANT PLOTS.

During the 51-day test period, 21.59 in (0.55 m) of rainfall occurred. If an evaporation rate of only 10% were assumed, 19.4 in (0.49 m) or 5.2×10^5 gal (197 m^3) of rainfall could have left the area as soil/water percolate (assuming direct water runoff was negligible). The evaporation rate is known to be higher than 10%, based on average evaporation rates for the area, as reported by TVA, and it is known that surface runoff occurred. However, the assumption of 10% evaporation and no runoff water was made so that the highest expected oil and coolant losses could be calculated. Each treatment area represents approximately 0.3 acre ($3 \times 10^2 \text{ m}^2$); thus, an assumed total water effluence via soil solution per treatment area was 1.5×10^5 gal ($5.7 \times 10^2 \text{ m}^3$) or 1.2×10^6 lb (545 Mg) of water during the test period from May 13 to August 19.

Nitrate losses from the control areas (Figure 9) could logically be expected to be higher than from oily waste areas since fertilizer was added, but microbial immobilization would be low due to lack of carbon substrate. The organic carbon loss from control plots was higher than normally observed in virgin forest areas. Since the lysimeters, by necessity, were located near the edge of the plots, the higher-than-expected carbon loss from the control plots could reflect some degree of lateral movement of oily wastes.

While these data are variable, they do support the conclusions that very little loss or organic carbon has occurred in the percolate water flow [ie, 17.46 lb (7.9 kg) of oil and 110.7 lb (50.3 kg) of coolant in the 57-day test period].

Evolution of Carbon Dioxide Gas

A mobile carbon dioxide (CO_2) analysis instrument was placed at the oil and coolant plots in order to obtain the rate of CO_2 being evolved from the plots. This instrument has ten

programmed sampling lines, each of which is connected to a chamber which was placed over the soil that was sampled. Sample locations in the plots included the noncontaminated control plots for use as background data. Continuous monitoring of the area was made for one 24-hour and two 72-hour periods.

The first samples were collected on May 21 and showed a CO₂ evolution rate from Plots 1 and 2 which was equivalent to an oil decomposition rate of 9.3 lb (4.2 kg) per acre ($4 \times 10^3 \text{ m}^2$) per day. The machine coolant plots showed an equivalent oil decomposition rate of 8 lb (3.6 kg) per acre ($4 \times 10^3 \text{ m}^2$) per day, as determined by CO₂ evolution rates. Spot samples taken from the area showed a low microbial population of 1.5×10^6 organisms per gram of soil. Fertile soil normally has a population of 5×10^9 organisms per gram of soil.

During the second sample period of June 26 and 27, the CO₂ evolution rates had increased and a loss of 31.2 lb (14 kg) of oil per acre ($4 \times 10^3 \text{ m}^2$) per day was noted. Prior to these samples, the plots had been fertilized in order to obtain a calculated carbon-to-nitrogen ratio of 230:1.

The third sampling period (June 23 through 25) showed a CO₂ evolution rate equivalent to 50 lb (23 kg) of oil per day per acre ($4 \times 10^3 \text{ m}^2$). During this sampling period, rainfall occurred and an oil decomposition rate of 109 lb (49 kg) of oil per acre ($4 \times 10^3 \text{ m}^2$) per day was noted for a few hours after the rainfall. A CO₂ rate equivalent to 50 lb (23 kg) of oil per acre ($4 \times 10^3 \text{ m}^2$) per day is 1.8 times greater than the CO₂ evolution from forest soil.

The CO₂ gas data obtained on a minimal basis do not show that large amounts of oil are being decomposed. A decomposition rate of 50 lb (23 kg) per day per acre ($4 \times 10^3 \text{ m}^2$) would be equal to about 7 gal (0.026 m³) of oil per day per acre ($4 \times 10^3 \text{ m}^2$). Chemical analyses of the soil indicate that about 2600 gal (98 m³) of oil had decomposed in Plots 1 and 2 during the 54-day test period (June 6 - August 1). Also, machine coolant was decomposed at a rate of about 840 gal (32 m³) of oil per week [$\sim 5900 \text{ gal}$ (22.3 m³) of oil during the test period].

Evaporation of Organics

Laboratory tests were conducted to determine the amount of oil and coolant lost to the atmosphere by evaporation from the test plots. For these tests, 4.1-kg samples of the oil/soil mixture from the test plots were taken immediately after application of oil and coolant. These 4.1-kg samples were placed in a closed cylinder with a soil depth of approximately one inch (0.02 m). Nitrogen or air was monitored into the cylinder and the evaporated condensables were collected during a two-hour test period in a dry ice, acetone-cooled tube. The condensed material was measured and analyzed for total organic carbon (TOC). Results of these tests are reported in Tables 12 and 13.

Waste Oil - These data (Table 12) show that an oil/soil sample evolved water which contained a maximum level of 105 $\mu\text{g/ml}$ TOC. As expected, the amount of water which was evaporated was dependent on the gas flow rate. The TOC values also decreased with increased test times. A calculated loss of oil from the oil plots (Plots 1 and 2), as a function of the test time, is given in Figure 10. These data show that, during the first day, 1.7 lb (0.8

Table 12
EXPERIMENT 1 - PLOTS 1 AND 2
(Oil Applied - 4.1 Kilograms)

Elapsed Time ⁽¹⁾ (hr)	Purge Gas	Gas Flow		Condensed Water/Oil Mixture (g)	Total Organic Carbon ($\mu\text{g/ml}$)	Normalized Data to a Constant Flow of 3100 cc/min		
		(cc/min)	($\mu\text{m}^3/\text{s}$)			Condensed Water/Oil Mixture (g)	Estimated Oil Losses from 0.3 Acre	
2	N ₂	333	5.5	2.5	105	23.3	0.32	0.14
4	N ₂	200	3.3	1.3	105	20.2	0.28	0.13
6	N ₂	80	1.3	0.7	90	27.1	0.32	0.14
8	N ₂	1400	23.3	7.4	75	16.3	0.16	0.07
10	Air	4500	75.0	14.8	61	10.2	0.08	0.04
12	Air	3100	51.7	13.3	77	13.3	0.13	0.06
14	Air	3100	51.7	15.5	39	15.5	0.08	0.04
30	Air	3100	51.7	5.0	45	5.0	0.02	0.01

(1) Gas was passed over the sample for two hours for each test.

Table 13
EXPERIMENT 2 - PLOTS 3 THROUGH 6
(Machine Coolant Applied - 4.1 Kilograms)

Elapsed Time ⁽¹⁾ (hr)	Gas Flow		Condensed Water-Oil Mixture (g)	Total Organic Carbon ($\mu\text{g/ml}$)	Normalized Data to a Constant Flow of 5700 cc/min		
	(cc/min)	($\mu\text{m}^3/\text{s}$)			Condensed Water-Oil Mixture (g)	Estimated Oil Losses from 0.6 Acre	
2	6070	101	10.8	160	10.1	2.14	1.0
4	1600	27	9.0	173	32.0	7.32	3.3
6	4050	67	9.5	184	13.4	4.6	2.1
8	5700	95	10.3	98	10.3	1.32	0.6
28	5700	95	7.2	48	7.2	0.46	0.2

(1) Gas was passed over the sample for two hours for each test.

kg) of oil could be lost through evaporation to the ambient air. Since the loss rate decreases with test time, an estimated loss by evaporation from June 6 through August 1 would be less than 2.5 lb (1.1 kg) of oil if the ambient temperatures and wind velocity in Plots 1 and 2 were similar to the test conditions.

A second method of estimating the oil loss by evaporation in Plots 1 and 2 was to assume that the water evaporated contained 105 $\mu\text{g/g}$ of oil, which was the maximum noted in the laboratory. During June 6 through August 1, the normal evaporation rate for this period was approximately 10 in (0.2 m), based on area evaporation data collected by TVA for the period 1942 through 1969. Evaporation of 10 in (0.25 m) of water in Plots 1 and 2 would be the equivalent evaporation of about 80,000 gal (303 m^3) of water. If the evaporated water contained 105 $\mu\text{g/ml}$ TOC, such as found in laboratory experiments, the total oil evolved from Plots 1 and 2 during a 53-day test period would be 8.4 gal ($3.2 \times 10^{-2} \text{ m}^3$).

Figure 10. OIL VAPORIZED FROM OIL/SOIL SAMPLE. (Experiment 1)

In summary, the amount of oil believed to have evaporated from Plots 1 and 2 was insignificant. During a 53-day test period, 9700 gal (36.7 m^3) of oil was applied to Plots 1 and 2. If 8.4 gal ($3.2 \times 10^{-2} \text{ m}^3$) were lost by evaporation, the evaporation losses would be less than 0.1% of the oil applied to these plots.

Machine Coolant - Laboratory tests were also conducted to determine the amount of oil which may be evaporated from the machine coolant (Plots 3 through 6). Soil from these plots was taken immediately after the coolant was spread over the soil. The soil was placed in a sealed container similar to the oil/soil tests. The water evaporated from the soil was collected and analyzed for TOC. The maximum TOC value found to date has been 184 $\mu\text{g/ml}$. Results of the coolant tests are listed in Table 13.

These data show that a coolant/soil sample evolved water which contained a maximum level of 184 $\mu\text{g/ml}$ TOC, and the TOC values decreased with increased test times. A calculated loss of coolant oil from the coolant (Plots 3 through 6), as a function of time, is given in Figure 11. These data show that a total loss of 37 lb (16.7 kg) [ie, 4.6 gal ($1.7 \times 10^{-2} \text{ m}^3$)] could be lost through evaporation during the first day after coolant had been applied to the soil. The losses decrease with time, and an estimated oil loss by evaporation for a seven-day period would be less than 42 lb (19 kg) [5.3 gal ($2 \times 10^{-2} \text{ m}^3$)] of evaporated oil from Plots 3 through 6. Fresh coolant was spread on these plots approximately once per week from June 6 through August 1. It could be assumed that total loss during the seven-week test period may have been approximately 294 lb (133 kg) [7 weeks $\times$ 42 pounds per week] which is equal to 36.7 gal ($1.4 \times 10^{-1} \text{ m}^3$).

A second method of estimating the coolant loss by evaporation in Plots 3 through 6 is to assume that all water evaporated from the plots contains a TOC level of $184 \mu\text{g/ml}$. If 10 in (0.025 m) of water evaporated during June 6 through August 1, the oil losses would be 232 lb (105 kg) or 29 gal ($1.1 \times 10^{-1} \text{ m}^3$).

In any event, the loss of oil by evaporation was not considered to be significant since a total of 25,500 gal (96 m^3) of coolant [ie, equivalent to 5900 gal (22 m^3) of oil] were applied to Plots 3 through 6 during the May 18 - August 1 test period. An evaporation loss of either 29 or 36.7 gal (0.11 or 0.14 m^3) would be less than 0.6% loss by evaporation.

Figure 11. MACHINE COOLANT VAPORIZED FROM COOLANT/SOIL SAMPLE. (Experiment 2)

Soil Carbon Content

Periodic composite sample analyses of waste oil (Plots 1 and 2) and machine coolant (Plots 3 through 6) are presented in Tables 14 and 15. Typical analyses of oily wastes applied are presented in Tables A-6 and A-7, Appendix A. The laboratory technique for determining carbon and hydrogen in soil samples by the combustion method is described in Appendix B. Using these data, calculations were made to determine the oil carbon applied to the plots. These values were then compared with the carbon determined to be present in soil samples, less the naturally occurring soil carbon. These data are shown graphically for the oil and coolant plots in Figures 12 and 13, respectively.

Table 14
SOIL SAMPLE ANALYSES FOR WASTE OIL PLOTS 1 AND 2

Date (1973)	Cumulative Oil		Moisture (%)	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Uranium ($\mu\text{g/g}$)
	(lb)	(Mg)					
May 14	None		4.96	0.80	0.64	-	1
May 22 ⁽¹⁾	51,400	23	13.82	8.02	-	-	24
June 4	51,400	23	10.34	7.39	1.57	-	19
June 26	51,400	23	9.63	5.30	1.15	-	-
July 10	51,400	23	6.09	5.00	1.13	-	-
July 12	71,840	33	7.18	7.75	1.52	-	-
August 6	71,840	33	11.06	5.93	1.30	-	9
August 20	71,840	33	5.02	5.02	1.21	-	-
September 4	71,840	33	3.88	5.84	1.27	0.0964 ⁽²⁾	17
September 6	71,840	33	7.97	6.09	1.26	-	76
September 14	110,980	50	15.18	10.37	1.59	-	84

(1) Date of first sample. First oil applied on May 16 and 21.

(2) Total nitrogen, all forms in soil.

Table 15
SOIL SAMPLE ANALYSES FOR MACHINE COOLANT PLOTS 3 THROUGH 6

Date (1973)	Cumulative Oil		Moisture (%)	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Uranium ($\mu\text{g/g}$)
	(lb)	(Mg)					
May 14	None		4.96	0.80	0.64	-	1
May 22(1)	32,720	15	15.40	2.78	-	-	140
June 4	32,720	15	9.35	2.37	0.97	-	85
June 26	139,740	63	11.41	2.98	0.95	-	-
July 10	164,090	74	10.87	3.30	1.07	-	-
August 6	240,090	109	12.43	3.14	1.03	-	106
September 20	390,450	177	20.20	3.51	1.04	-	-
September 27	418,470	190	13.70	3.78	1.10	-	-

(1) Date of first sample. First coolant applied on May 18.

Figure 12. SOIL CARBON LEVELS IN PLOTS 1 AND 2.

During the first 50-day period subsequent to the first sampling, there was a 43.2 wt % carbon reduction in waste oil (Experimental Plots 1 and 2) and 20.0 wt % in coolant (Plots 3 through 6). Cumulative carbon reduction up to the 116th day in Plots 1 and 2 (Figure 12)

Figure 13. SOIL CARBON LEVELS IN PLOTS 3 THROUGH 6.

was 40.05 wt %, indicating a reduction of 32,491 lb (15 Mg) of oil carbon. This loss was equivalent to 8400 lb (3.8 Mg) of oil carbon per month, or 1.1 lb (0.5 kg) of oil carbon per ft^3 (0.03 m^3) per month, which is equivalent to 1.5 lb (0.7 kg) of oil per ft^3 (0.03 m^3) per month. This rate is in agreement with the experimental work of Kincannon⁽⁴⁾ at the Shell Oil Company's Houston Refinery. Cumulative carbon reduction in coolant (Plots 3 through 6) was 25.8 wt % at the end of 122 days. These data indicate that 10,448 lb (4.7 Mg) of coolant carbon were assimilated in 122 days, equivalent to 2570 lb (1.2 Mg) per month or 0.342 lb (0.16 kg) coolant carbon per ft^3 (0.03 m^3) per month, which is equal to 4.45 lb (2 kg) of coolant per ft^3 (0.03 m^3) per month. If organic residues are converted to humus, which functions as a soil builder and increases the level of the baseline carbon value, the actual decomposition of the oily wastes may be even higher than the carbon concentrations suggest.

OBSERVATIONS, CONCLUSIONS, AND RECOMMENDATIONS

OBSERVATIONS

After four months of large-scale field tests, the following observations were made:

1. Oil wastes and machine coolants were decomposed by mixing with soil in cultivated plots where naturally occurring microorganisms metabolize the oily wastes.
2. Applications of agricultural lime and fertilizer are desirable for maintenance of pH control and to supply nutrient materials for microbial growth. Application rates were 1600 to 1700 lb (726 to 772 kg) per acre ($4 \times 10^3 \text{ m}^2$) for nitrogen and 350 to 450 lb (159 to 204 kg) for potassium and phosphorus during the four-month period.
3. Intermittent cultivation was desirable to promote aerobic conditions in the top 6-in (0.15-m) soil layer for maximum microbial response.
4. During extremely dry weather, irrigation with neutralized nitrate effluents was found to be beneficial.
5. Frequent small applications of oil and coolant produced better overall responses than single, large applications. Cultivation was resumed earlier and surface rainwater runoff was drained out of the cultivated plots with less apparent loss of oil and nutrients. Heavy applications, followed by rainfall, produced ponding conditions leading to anaerobic conditions with attendant odors and slimes.
6. Continued cultivation with tractor-pulled equipment produced an impervious hard pan layer below the six-inch cultivation zone, which limited infiltration of oil and nutrients but could have deprived the upper cultivated soil layer from receiving moisture rising through the subsoil layers by capillary action in dry weather. During the test period, the hard pan layer appeared to be an advantage, but could be broken with an implement known as a subsoiler.
7. Soil percolate water samples, surface rainfall runoff, and nine-foot test well samples all indicated a minimal loss of organic carbon and nutrients, although considerable variability existed due to frequency and intensity of rainfall after applications of oily wastes.
8. Carbon dioxide respiration rate measurements showed a loss rate of 50 to 100 lb (23 to 46 kg) of oil per day per acre ($4 \times 10^3 \text{ m}^2$).
9. Soil carbon analyses indicated a loss rate of approximately 1.1 lb (0.5 kg) of organic carbon per ft^3 (0.03 m^3) per month for waste oil (ie, $\sim 384 \text{ gal/day/acre}$) and 0.34 lb (0.15 kg) for machine coolant (ie, $\sim 594 \text{ gal/day/acre}$). These analyses do not reflect the organic carbon that was permanently added to the soil in the form of humus, which could account for higher assimilation rates.
10. Volatile products resulting from evaporation were minimal and not readily detectable. Limited analyses indicated that the primary evaporative constituents are those identified with oils and coolants.

11. A strict material balance cannot be made from the test data at this time. The carbon loss rate as indicated by laboratory analysis was significantly higher than indicated by the evaporation losses, runoff and percolate losses, and the CO₂ evolution rates. Development studies will continue in order to obtain a more satisfactory material balance.

CONCLUSIONS

Laboratory and small-scale field tests provided the following conclusions:

1. Uninhibited vacuum pump oils were converted to carbon dioxide and water by biodegradation.
2. Small field tests showed that 330 gal (1.2 m³) of used vacuum pump oil could be mixed with about 60 ft³ (1.7 m³) of earth and biodegraded by utilizing in situ bacteria. No evidence of free oil was released from the soil over a period of seven months, despite extremely heavy rainfall during this period.
3. Similarly, 600 gal (2.3 m³) of used machine coolant were mixed with 60 ft³ (1.7 m³) of earth. No detectable oil was released from the site over the seven-month period.
4. Emulsions of oil and water (coolant) were separated in the laboratory by passing the emulsion through a column of soil. Oil was retained by the soil and the water passed through the column.
5. Chemical analyses of used oil were conducted to determine the quantities and types of impurities which, if released, could have an impact upon the environment, depending on the disposal method utilized.
6. An analytical method to determine carbon and hydrogen in soil was developed by the Special Mass Spectrometry Laboratory.
7. Waste oil and nitrate solutions were successfully distributed over a 0.088-acre (356-m²) experimental plot using conventional irrigation spray equipment. Analyses indicated that approximately 70% of the oil was biologically decomposed within three weeks. Samples of percolate water discharging from an underlying drain tile indicated a minimal loss of oil, but an appreciable loss of nitrate ion in a 33-day period immediately following the oil/nitrate application. Precipitation amounting to 7.9 inches (0.2 m) fell during this period, resulting in a continuous flow of percolate water from the experimental plot which might be considered one of the most unfavorable conditions to be anticipated.

RECOMMENDATIONS

As a result of this study, the following recommendations are made:

1. Although microbial responses were obtained during favorable summertime climatic conditions, field tests should be continued throughout the winter and spring months when inclement weather may have an adverse effect on the microbial response.

2. Heavier applications of nitrate fertilizer nutrient are recommended to achieve lower carbon-to-nitrogen ratios; thus, inducing greater microbial assimilation.
3. Further investigation of the evaporation losses and the identification of these compounds is recommended to insure that no obnoxious or toxic substances enter the environment.

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APPENDIX A

CHEMICAL ANALYSES DATA

Table A-1
ANALYSIS OF USED OILS
(All Values in µg/ml)

Element	Vacuum Pump Oil		Crankcase Oil	Surface Oil-Field Pond 2	
	Filtered	Unfiltered	Unfiltered	Filtered	Unfiltered
Be	< 0.005	< 0.01	< 0.01	< 0.01	< 0.01
B	0.02	0.3	6.0	0.3	0.2
F	0.09	0.3	0.3	0.3	0.3
Na	100.0	20.0	500.0	50.0	20.0
Mg	0.3	1.0	10.0	1.0	1.0
Al	4.0	4.0	4.0	20.0	1.0
Si	10.0	10.0	80.0	80.0	1,500.0
P	0.2	0.7	1,500.0	6,000.0	14,500.0
S	2.0	10.0	40.0	20.0	7.0
Cl	200.0	650.0	1,000.0	1,000.0	2,000.0
K	2.0	2.0	20.0	20.0	2.0
Ca	3.0	9.0	3,000.0	9.0	3.0
Sc	0.6	< 0.06	0.2	< 0.06	< 0.06
Cr	0.1	< 0.09	0.9	< 0.09	< 0.09
Mn	0.1	0.1	0.8	< 0.08	< 0.08
Fe	80.0	40.0	80.0	10.0	30.0
Ce	0.08	< 0.08	< 0.08	< 0.08	< 0.08
Ni	0.2	0.2	0.2	< 0.1	< 0.1
Cu	0.4	0.6	0.2	< 0.1	< 0.1
Zn	2.0	6.0	300.0	6.0	2.0
Cd	0.3	< 0.5	< 0.5	< 0.5	< 0.5
Sn	< 0.2	< 0.5	< 0.5	< 0.5	< 0.5
Ba	0.3	< 0.3	150.0	1.0	< 0.3
Ta	0.8	< 0.8	< 0.3	< 0.3	< 0.3
W	0.4	< 0.8	< 0.8	< 0.8	< 0.8
Hg	< 0.3	< 0.9	< 0.9	< 0.9	< 0.9
Pb	< 0.2	< 0.6	200.0	< 0.6	< 0.6
Bi	< 0.1	< 0.3	< 0.3	< 0.3	< 0.3
Th	0.5	0.5	< 0.3	< 0.3	< 0.3
U	< 0.1	< 0.3	< 0.3	< 0.3	< 0.3
Mo	< 0.6	< 0.6	20.0	< 0.6	< 0.6

Table A-2
SPECTROCHEMICAL ANALYSES OF INITIAL
SOIL SAMPLE PRIOR TO APPLICATION
OF OIL OR NITRATE
(All Values in %)

Spectrographic Analyses			
Element	Element		
Ag	< 0.01	Mo	0.002
Al	20.0	Na	0.03
Au	< 0.02	Nb	< 0.02
B	0.08	Ni	0.01
Ba	0.04	P	< 1.0
Be	< 0.001	Pb	< 0.01
Bi	< 0.01	Pd	< 0.002
Ca	0.15	Pt	< 0.02
Co	< 0.005	Sb	< 0.04
Cr	< 0.04	Si	> 20.0
Cs	< 0.6	Sn	< 0.005
Cu	0.005	Ta	< 0.15
Fe	8.0	Th	< 0.04
Hf	< 0.02	Ti	0.6
K	1.2	V	< 0.005
Li	< 0.02	W	< 0.08
Mg	2.0	Zn	< 0.08
Mn	0.08	Zr	0.04
Chemical Analyses			
C	0.445	NO ₃	0.0031
U	0.0001	NH ₃	0.0053
pH	3.83		

(1) Note: Sampled on 10-2-72 after site preparation.

Table A-3
SPECTROCHEMICAL ANALYSES OF PERCOLATE
WATER FROM EXPERIMENTAL PLOT
SUBSEQUENT TO 1.40 INCHES OF
RAINFALL AND PRIOR TO OIL-
NITRATE APPLICATION
(All Values in µg/ml)

Spectrographic Analyses			
Element	Element		
NO ₃ ⁽¹⁾	20.0	Mn	0.01
Ag	< 0.01	Mo	< 0.01
Al	0.8	Na	2.0
As	< 0.01	Nb	< 0.01
Au	< 0.01	Ni	0.04
B	< 0.01	P	< 1.0
Ba	0.4	Pb	< 0.01
Be	< 0.01	Pd	< 0.01
Bi	< 0.1	Rb	< 0.2
Ca	12.0	Rh	< 0.01
Cd	< 0.01	Ru	< 0.01
Co	< 0.2	Sb	< 0.01
Cr	0.1	Sc	< 0.01
Cs	< 0.6	Si	2.0
Cu	< 0.1	Sn	< 0.01
Fe	0.4	Ta	< 1.0
Ga	< 0.01	Th	< 0.04
Ge	< 0.01	Ti	< 0.01
Hf	< 0.01	Tl	< 0.01
Hg	< 0.01	U ⁽²⁾	< 0.01
In	< 0.01	V	< 0.01
Ir	< 0.02	W	< 0.1
K	< 0.2	Y	< 0.01
Li	0.8	Zn	< 0.6
Mg	10.0	Zr	< 0.02

(1) Ultraviolet spectrophotometric method of analysis.

(2) Fluorimetric method of analysis; sampled 10-2-72.

Table A-4
SPECTROCHEMICAL ANALYSES OF LIME-HYDRATE-
NEUTRALIZED NITRATE SOLUTION USED
FOR OIL TEST PLOT
(All Values in µg/ml)

Spectrographic Analyses			
Element	Element		
Ag	< 0.1	Mo	< 0.1
As	< 0.1	Nb	< 0.1
Au	< 0.1	Ni	1.0
B	0.1	P	< 1.0
Ba	1.0	Pb	< 0.1
Be	< 0.1	Pd	< 0.1
Bi	< 1.0	Rb	< 1.0
Cd	< 0.4	Sb	< 0.1
Co	< 0.06	Sc	< 0.1
Cr	< 0.1	Si	1.0
Cs	< 0.0	Sn	< 0.1
Cu	0.04	Ta	< 1.0
Fe	< 2.0	Ti	< 0.1
Ga	< 0.1	Tl	< 0.1
Ge	< 0.1	V	< 0.1
Hf	< 1.0	W	< 1.0
In	< 0.1	Y	< 0.1
Ir	< 0.1	Zn	< 1.0
Li	30.0	Zr	< 0.1
Mn	30.0		
Chemical Analyses			
Al	6.0	Cl	22.8
Ca	2,750.0	CO ₂	23.0
K	65.0	HCO ₃	65.0
Mg	300.3	NO ₃	10,896.0
Na	140.0	SO ₄	17.2
Th	0.37	PO ₄	< 0.1
U	0.27		
Other Properties			
pH	6.74	Sp Gr	1.010

Table A-5
EFFECT OF RAINFALL ON OIL-NITRATE IRRIGATED ON PLOT 1

Date (1972)	Bear Creek Rainfall		Percolate		Percolate		Oil (wt %)	Oil		Nitrate (μg/ml)	Nitrate		Uranium (μg/g)	pH
	(in)	(cm)	(gpm)	(10 ⁻⁵ m ³ /s)	(lb/day)	(kg/day)		(lb/day)	(kg/day)		(lb/day)	(kg/day)		
10-12	0.14	0.36	0.0	0										
10-13	0.90	2.3	1.0	6.3	12,000	5,450	0.66	79.21	36	282	3.384	1.5	0.02	7.46
10-14	-	-	0.1	0.6	1,200	545	3.33	40.0	18	141	0.169	0.08	0.05	7.86
10-15	-	-	0.01	0.06	120	55	0.30	0.4	0.18	73	0.009	0.004	0.03	7.28
10-16	0.36	0.91	0.01	0.06	120	55	0.10	0.1	0.05	54	0.006	0.003	0.05	7.23
10-17	1.74	4.4	2.0	12.6	24,000	11,000	0.02	4.8	2.2	45	1.080	0.49	0.02	6.95
10-18	1.34	3.4	3.71	23.4	44,520	20,000	0.005	2.2	1.0	131	5.832	2.65	0.02	6.55
10-19	0.60	1.52	3.32	20.9	39,840	18,000	0.005	2.0	0.9	64	2.550	1.15	< 0.01	6.92
10-20	-	-	0.20	1.3	2,400	1,100	0.14	2.96	1.3	91	0.218	0.10	< 0.01	7.35
10-21	-	-	0.07	0.44	840	380	0.01	0.03	0.01	67	0.056	0.025	< 0.01	7.10
10-22	-	-	0.04	0.25	480	220	0.006	0.03	0.01	39	0.019	0.009	0.06	7.40
10-23	0.18	0.46	0.03	0.18	360	160	0.006	0.02	0.01	26	0.009	0.004	0.05	7.63
10-24	-	-	0.05	0.31	600	270	0.10	0.60	0.27	39	0.023	0.010	0.05	7.44
10-25	-	-	0.05	0.31	600	270	0.16	0.96	0.44	36	0.022	0.010	0.05	7.87
10-26	-	-	0.03	0.18	360	160	0.02	0.07	0.03	20	0.007	0.003	0.08	7.63
10-27	0.48	1.2	0.02	0.12	240	110	0.04	0.10	0.05	11	0.003	0.001	0.08	7.93
10-28	0.08	0.20	0.44	2.8	5,280	2,400	0.03	1.56	0.71	75	0.396	0.180	0.02	6.80
10-29	-	-	0.09	0.57	1,080	490	0.08	0.86	0.39	55	0.059	0.026	0.04	7.14
10-30	0.04	0.10	0.04	0.25	480	220	0.09	0.43	0.19	35	0.017	0.008	0.04	7.64
10-31	0.10	0.25	0.04	0.25	480	220	0.10	0.48	0.22	43	0.021	0.010	0.04	7.25
11-1	-	-	0.05	0.31	600	270	0.05	0.30	0.14	29	0.017	0.008	0.05	7.66
11-2	0.28	0.71	0.03	0.18	360	160	0.04	0.14	0.06	21	0.008	0.004	0.06	7.90
11-3	-	-	0.10	0.63	1,200	545	0.07	0.84	0.38	57	0.068	0.003	0.02	7.73
11-4	-	-	0.05	0.31	600	270	0.05	0.30	0.14	35	0.021	0.010	0.03	7.71
11-5	-	-	0.03	0.18	360	160	0.02	0.07	0.03	14	0.005	0.002	0.04	7.82
11-6	-	-	0.02	0.12	240	110	0.02	0.05	0.02	7	0.002	0.001	0.04	7.93
11-7	1.07	2.7	0.02	0.12	240	110	0.02	0.05	0.02	5	0.001	0.001	0.04	7.90
11-8	-	-	0.41	2.6	4,920	2,200	0.03	1.47	0.67	43	0.212	0.096	0.01	7.37
11-9	-	-	0.09	0.57	1,080	490	0.02	0.22	0.10	28	0.030	0.014	0.02	7.53
11-10	0.11	0.28	0.04	0.25	480	220	< 0.01	0.05	0.02	32	0.015	0.007	0.02	7.97
11-11	-	-	0.05	0.31	600	270	< 0.01	0.06	0.03	32	0.019	0.009	0.02	8.06
11-12	-	-	0.04	0.25	480	220	0.02	0.10	0.05	20	0.009	0.004	0.02	7.60
11-13	0.45	1.1	0.03	0.18	360	160	0.03	0.11	0.05	12	0.004	0.002	0.02	7.60
11-14	0.03	0.08	0.15	0.95	1,800	820	0.04	0.72	0.33	24	0.043	0.020	0.02	7.40
11-15	-	-	0.04	0.25	480	220	0.02	0.10	0.05	10	0.005	0.002	0.02	7.50

Table A-6
TYPICAL COMPOSITION OF OILY WASTES

Description	Density		C (%)	H (%)	U ($\mu\text{g/g}$)
	(lb/gal)	(kg/cm^2)			
Waste Oil Composite	7.41	0.9	73.10	11.73	4
Machine Coolant Composite	8.15	1.0	12.40	7.43	23
Machine Coolant and Mop Water Mixed	8.26	1.0	3.30	7.41	35
Waste Oil from Ponds	7.40	0.9	83.01	12.79	49

Table A-7
SPECTROGRAPHIC ANALYSES OF OILY WASTES

Element	Waste Oil Composite (%)	Machine Coolant Composite (%)	Mixture of Machine Coolant and Mop Water (%)	Waste Oil from Ponds (%)
Ag	< 0.000001	< 0.00001	< 0.00002	< 0.002
Al	0.0002	0.0008	0.001	0.005
Au	-	0.00004	< 0.00008	< 0.001
B	0.00002	0.00008	0.001	0.0005
Ba	0.00004	0.002	0.00008	0.0002
Be	0.0012	0.00004	0.000004	< 0.00005
Bi	-	< 0.00002	0.00004	< 0.0005
Ca	0.0025	0.004	0.02	0.008
Cd	0.00002	< 0.00004	< 0.0002	< 0.002
Co	< 0.00002	0.00002	< 0.00002	< 0.0002
Cr	0.0002	0.0001	0.0002	< 0.0005
Cs	-	< 0.001	< 0.002	< 0.03
Cu	0.00005	0.0002	0.0003	< 0.0002
Fe	0.0009	0.002	0.007	0.03
Ge	-	-	-	-
Hf	-	< 0.00004	< 0.00008	< 0.001
K	0.0050	< 0.04	0.08	< 0.002
Li	0.00045	0.0001	0.0002	< 0.001
Mg	0.00045	0.0006	0.002	0.001
Mn	0.00005	0.00004	0.00008	0.001
Mo	0.000001	0.00002	0.0002	< 0.0001
Na	> 0.0200	> 0.04	0.08	0.001
Nb	-	0.00004	0.0003	< 0.001
Ni	< 0.000004	< 0.00002	0.00008	< 0.0005
P	< 0.0001	0.02	< 0.004	0.05
Pb	0.00004	0.0003	0.0003	< 0.0005
Pd	-	0.000004	-	-
Rb	-	0.0003	< 0.006	< 0.008
Sb	-	< 0.00008	< 0.0002	< 0.002
Si	0.00045	0.001	0.005	0.01
Sn	< 0.000001	0.001	< 0.00002	< 0.0002
Ta	-	< 0.0003	0.006	< 0.008
Th	-	< 0.00008	< 0.0002	< 0.002
Ti	0.00002	0.00008	0.0002	< 0.0005
U	0.0060	0.002	0.008	< 0.02
V	< 0.000001	0.00001	0.00002	< 0.0002
W	< 0.00001	0.0003	0.0006	< 0.004
Zn	0.0002	< 0.0002	< 0.0003	< 0.004
Zr	0.00015	0.00002	0.0002	0.0001

Table A-8
RAINFALL AND OIL-PLOT EFFLUENT DATA FOR MAY 1973

Date (May 1973)	Rainfall		Description of Sample	Estimated Surface Runoff		pH	NO ₃ (μg/ml)	Total Organic Carbon (μg/ml)	U (μg/g)
	(in)	(cm)		(gpm)	(μm ³ /s)				
17	0.33	0.8	No Surface Drainage	None					
19	0.38	1.0	Plots 1 - 3, East End	0.02	1.2	7.4	2	11	0.37
20			Plots 1 - 3, East End	0.02	1.2	7.4	1	12	0.35
23	0.88	2.2							
24	0.38	1.0	Plots 1 - 3, West End	2.0	120	7.5	113	32	
			Plot 3, East End	0.02	1.2	8.1	12	25	
			Branch Water North of Oil Farm	10.0	600	7.7	4	25	
			Branch Water East of Oil Farm	2.0	120	8.1	3	14	
25			Plot 2, Pond West End	None		6.7	137	50	0.01
			Plot 4, East End	0.1	6	7.1	34	108	0.01
			Plot 5, East End	0.5	30	8.0	10	1	
26	0.34	0.9							
27	4.40	11.1	Plots 1 - 3, West End	20	1200	7.1	13	11	0.01
28			Plots 1 - 3, West End	0.2	12		12	28	0.01
			Plots 1 - 3, East End	0.02	1.2		6	10	0.01
29			Plots 1 - 3, West End	0.2	12		58	15	
			Drainage	10.0	600	7.2	76	60	
			Plots 1 - 3, East Pond Drainage	20.0	1200	7.1	35	46	
30	0.11	0.28							
31			Plots 1 - 3, East End	0.02	1.2		1	42	
			Plots 1 - 3, West End	0.03	1.8		1	1	
			Sanitary Landfill Pit	30.0	1800	6.9	3	5	

Table A-9
RAINFALL AND OIL-PLOT EFFLUENT DATA FOR JUNE 1973

Date (June 1973)	Rainfall		Description of Sample	Surface Runoff		pH	NO ₃ (μg/ml)	Total Carbon (μg/ml)	Total Organic Carbon (μg/ml)	U (μg/g)
	(in)	(cm)		(gpm)	(μm ³ /s)					
1	0.08	0.2								
5	0.47	1.2								
6	1.16	2.9	Plot 4, West End	5.0	300	7.0	96	461	400	0.13
			Plot 4, East End	2.0	120	7.3	17	284	204	0.10
			Plots 1 - 4, West End	0.01	0.6		14	73	45	
7										
			Plots 1 - 4, East End	0.02	0.12		12	97	97	
13	0.13	0.3								
15	0.39	1.0								
16	1.46	3.7	Plots 1 - 4, East End	0.1	6	7.6	3	59	30	0.12
			Plots 1 - 4, West End	0.05	0.3	7.4	18	21	20	0.01
17	0.16	0.4								
18			Plots 1 - 4, East End	0.02	1.2	7.5	21	98	68	0.17
			Plots 1 - 4, West End	0.01	0.6	7.3	21	33	31	0.01
19	0.46	1.2								
20			Plots 3 and 4, East End	0.05	3	7.1	42	168	164	
20			Plots 3 and 4, West End	0.05	3	6.9	33	113	112	
21	0.56	1.4	Plots 1 - 6, East End Ditch			7.1	12	102	102	
21			Plots 1 - 6, West End Ditch			6.9		42	30	
21			West Ditch at Power Pole			6.9	30	22	17	
21			East Branch at Landfill	5.0	300	7.3	2	34	17	
25			East Branch at Landfill	5.0	300	7.3	1	38	29	
27	1.77	4.5								
28	0.05	0.1	West Ditch at Power Pole	0.05	3	7.2	50	77	75	
			East Branch at Landfill	20.0	1200	7.4	8	27	27	
29	0.27	0.7								

Table A-10
RAINFALL AND OIL-PLOT EFFLUENT DATA

Date (July 1973)	Rainfall		Sample Description and Location	Estimated Flow		pH	NO ₃ (μg/ml)	Total Carbon (μg/ml)	Total Organic Carbon (μg/g)
	(in)	(cm)		(gpm) ⁽¹⁾	(μm ³ /s)				
1	0.19	0.48	Percolate Water, East Branch			7.0			31
4	0.14	0.35							
7	0.41	1.0	Percolate Water, East Branch						19
8	0.03	0.07	Percolate Water, East Branch			7.0			21
9	0.02	0.05							
10	0.03	0.08							
14	1.04	2.6	Surface Runoff, Plots 1 - 6, West	5.0	300	7.0		57	44
			Surface Runoff, Plots 1 - 6, East	5.0	300	7.0		58	57
15	0.84	2.1							
16			Surface Runoff, Plots 1 - 6, West	0.01	0.6			40	40
			Surface Runoff, Plots 1 - 6, West	0.01	0.6			62	40
24	0.03	0.07							
25	0.55	1.4	Surface Runoff, Plots 1 - 6, West	5.0	300	7.1		36	32
			Surface Runoff, Plots 1 - 6, East	2.0	100	7.1		65	40
26	0.45	1.1	Surface Runoff, Plots 1 - 6, West	0.1	6			26	26
			Surface Runoff, Plots 1 - 6, East	0.1	6			22	22
27			Surface Runoff, Plots 1 - 6, West	2.0	100	7.0		93	92
			Surface Runoff, Plots 1 - 6, East	1.0	60	7.0		103	68
31	1.81	4.6	Surface Runoff, Plots 1 - 6, West	0.1	6	7.6	283	81	80
			Surface Runoff, Plots 1 - 6, East	0.1	6	7.1	738	160	148
TOTAL	5.54	14.1							

(1) The total volume of water is only approximated because the flow was not constant.

Table A-11
RAINFALL AND OIL-PLOT EFFLUENT DATA

Date (August 1973)	Rainfall		Sample Description and Location	Estimated Flow		pH	NO ₃ (μg/ml)	Total Carbon (μg/ml)	Total Organic Carbon (μg/g)
	(in)	(cm)		(gpm) ⁽¹⁾	(μm ³ /s)				
1	0.64	1.6	Surface Runoff, Plots 1 - 6, West	20	1200	7.6		106	95
			Surface Runoff, Plots 1 - 6, East	5.0	300	7.2		98	50
10	0.04	0.10							
12	0.06	0.15							
13	0.45	1.1							
14	0.26	0.66	Surface Runoff, Plots 1 - 6, West	0.1	6	7.1	15	93	32
			Surface Runoff, Plots 1 - 6, East	0.1	6	7.1	11	48	27
20	0.80	2.0							
TOTAL	2.25	5.7							

(1) The volume of water is not representative of a 24-hour day.

Table A-12
RAINFALL AND OIL-PLOT EFFLUENT DATA

Date (September 1972)	Rainfall		Sample Description and Location	Estimated Flow		pH	NO ₃ (μg/ml)	Total Carbon (μg/ml)	Total Organic Carbon (μg/g)
	(in)	(cm)		(gpm) ⁽¹⁾	(μm ³ /s)				
3			Percolate Water, East Branch	5.0	300	8.3	5	42	17
			Percolate Water, West Branch	2.0	120	6.8	8	50	23
9	0.15	0.41							
13	0.61	1.5							
14	0.24	0.61	Surface Runoff, Plots 1 - 6, East	2.0	120	7.3	95	82	58
			Surface Runoff, Plots 1 - 6, West	3.0	180	6.9	224	152	120
17	1.07	2.7	Surface Runoff, Plots 1 - 6, East	10.0	600		312	983	206
			Surface Runoff, Plots 1 - 6, West	20.0	1200		138	254	126
21	0.01	0.02							
23	0.12	0.30							
27	0.01	0.02							
29	1.16	2.9							
30	0.03	0.08							
TOTAL	3.41	8.7							

(1) Not representative of a 24-hour period.

Table A-13
SUMMARY OF NITRATE LOSSES IN SOIL WATER PERCOLATES

Date (1973)	Control Lysimeters ($\mu\text{g/ml NO}_3$)			Oil Plot Lysimeters ($\mu\text{g/ml NO}_3$)				Machine Coolant Lysimeters ($\mu\text{g/ml NO}_3$)			
	Sample 3	Sample 5	Average	Sample 1	Sample 2	Sample 4	Average	Sample 6	Sample 7	Sample 8	Average
June 6	3.94	154.5	79.2	2.74	216.9	1.99	73.9	33.6	2.04	1.82	12.4
June 15	2.92	390.1	197.0	0.49	67.3	2.57	23.5	8.4	1.20	1.33	3.6
June 22	1.15	151.6	76.6	0.62	1.5	0.49	0.8	303.7	NS(1)	0.75	152.3
June 28	0.09	148.7	74.4	3.63	3.8	0.22	2.6	58.0	1.15	0.44	19.9
July 5	0.09	188.2	94.3	0.58	NS	0.22	0.4	27.5	0.36	0.44	9.4
July 19	NS	NS	-	0.22	13.7	0.13	4.7	30.1	0.27	0.54	10.2
July 27	NS	359.5	-	0.75	13.7	0.13	4.9	162.0	0.88	0.49	54.5
August 1	2.66	321.6	162.0	0.22	NS	1.37	0.8	238.6	1.55	0.80	80.1

(1) NS - No sample. Indicative of low soil-water percolate.

Table A-14
SUMMARY OF ORGANIC CARBON LOSSES IN SOIL-WATER PERCOLATE

Date (1973)	Control Lysimeters ($\mu\text{g/ml TOC}$)			Oil Plot Lysimeters ($\mu\text{g/ml TOC}$)				Machine Coolant Lysimeters ($\mu\text{g/ml TOC}$)			
	Sample 3	Sample 5	Average	Sample 1	Sample 2	Sample 4	Average	Sample 6	Sample 7	Sample 8	Average
June 6	4.45	13.80	9.13	36.0	55.3	5.9	32.40	105.5	19.9	26.8	50.7
June 15	2.00	23.50	12.75	17.9	15.8	1.7	12.20	77.1	14.0	23.7	38.3
June 28	1.85	7.47	4.66	14.85	12.65	5.8	11.10	685.0	8.7	24.3	239.3
July 19	NS(1)	NS	-	10.65	17.55	3.28	10.50	213.0	5.0	23.6	80.6
July 27	3.71	8.91	6.30	9.37	14.10	3.44	8.97	118.0	3.0	26.3	49.1
August 1	9.00	11.15	10.08	18.35	NS	6.15	12.25	239.0	3.6	29.3	90.6

(1) NS - No sample. Indicative of low soil-water percolate.

APPENDIX B

DETERMINATION OF CARBON AND HYDROGEN IN SOIL BY THE COMBUSTION METHOD

Introduction

Carbon and hydrogen in soil samples can be determined simultaneously by the combustion method. In the classical analysis for carbon and hydrogen, the material is burned in a stream of oxygen (Figure B-1) to produce carbon dioxide and water. The two products are absorbed in appropriate reagents and weighed.

Figure B-1. CARBON COMBUSTION TRAIN.

Equipment and Materials

CO₂ absorber - Ascarite or Lithasorb.

Balance, analytical

Boats, combustion, ceramic, with covers - Preignited at 800° C for four hours.

Bubbler - A length of rubber hose with one end immersed in a small beaker half full of water.

Bulbs, absorption - Turner.

Copper oxide, wire form

Furnace, tube, hinged, 12 in (30.4 cm) long by 1 1/4 in (3.2 cm) ID - Equipped with pyrometers and Variacs.

Magnesium perchlorate, anhydrous

Oxygen supply - Equipped with an anhydrous magnesium perchlorate drying tube.

Poker, 24 in (61 cm) long - Made of 1/8-in (0.3-cm) stainless steel rod with a hook on one end and a plastic handle on the other.

Shot, tin

Stopper, rubber, Size 6, one hole - Containing a piece of 1/4-in (0.6-cm) glass tubing flush with the inner edge and extending a few inches from the outer edge.

Tube, combustion, quartz, 36 in (91 cm) long by 1 3/16 in (3.0 cm) OD - Exit end reduced to 1/4 in (0.6 cm) OD.

Tubing, seamless rubber, 3/16 in (0.5 cm) ID

Turnings, bright copper

Wool, glass

Assembly of Equipment

Combustion Tube -

- a. Loosely pack the first 6 in (15 cm) of the exit end of the combustion tube with bright copper turnings. Copper reduces the oxides of nitrogen to elemental nitrogen, eliminating a source of interference.
- b. Pack the next 10 in (25 cm) of the combustion tube with copper oxide, wire form. Copper oxide ensures complete oxidation of carbon and hydrogen.
- c. Insert the combustion tube into two tube furnaces which are placed end to end, with three inches (7 cm) of the exit end protruding.
- d. Insert the rubber stopper containing the glass tubing into the entrance end of the combustion tube and connect the glass tubing to the oxygen supply with rubber tubing.

Absorption Bulbs -

- a. Water Absorption Bulb. Place a 1/4-in (0.6-cm) layer of glass wool on the bottom, fill about 3/4 full with anhydrous magnesium perchlorate, and cover with a 1/4-in (0.6-cm) layer of glass wool.
- b. Carbon Dioxide Absorption Bulb. Place a 1/4-in (0.6-cm) layer of glass wool on the bottom, fill about 2/3 full with Ascarite or Lithasorb, cover with a 1/4-in (0.6-cm) layer of glass wool, add about 3/4 in (2 cm) of anhydrous magnesium perchlorate, and cover with a 1/4-in (0.6-cm) layer of glass wool. The magnesium perchlorate absorbs water liberated by the absorption of the carbon dioxide.
- c. Guard Bulb. Place a 1/4-in (0.6-cm) layer of glass wool on the bottom, fill about 2/3 full with anhydrous magnesium perchlorate, cover with a 1/4-in (0.6-cm) layer of glass wool,

add about 3/4 in (2 cm) of Ascarite or Lithasorb, and cover with a 1/4-in (0.6-cm) layer of glass wool. The guard bulb prevents atmospheric carbon dioxide and water from entering the train by diffusion or back pressure.

- d. Counterweights. To two absorption bulbs, add tin shot to adjust the weights to just below those of the water and carbon dioxide absorption bulbs, respectively.
- e. Connect the absorption bulbs with rubber tubing as illustrated in Figure B-1.

Maintenance -

- a. Periodically examine the combustion tube and absorption bulbs and replace the contents as indicated.
- b. Each time the train is disassembled for maintenance, recondition as described in the first two steps under Conditioning and Blanking.

Conditioning and Blanking

1. Adjust the temperature of both furnaces to 800° C with the Variacs.
2. Pass a low flow of oxygen through the train for 16 hours, or overnight.
3. Remove and close the water and carbon dioxide absorption bulbs.
4. Weigh the bulbs against the prepared counterweights.
5. Reconnect and open the absorption bulbs.
6. Connect the bubbler to the guard bulb, adjust the oxygen flow to 1 to 2 bubbles per second, and disconnect the bubbler.
7. Remove the stopper from the combustion tube and insert a boat containing 3 cm of copper oxide into the hot zone of the first furnace.
8. Allow to combust for 50 minutes.
9. Remove and close the water and carbon dioxide absorption bulbs.
10. Remove the spent boat from the combustion tube and replace the stopper to the combustion tube.
11. Reweigh the absorption bulbs against the prepared counter weights.
12. The blanks, or increase in weights of the bulbs, should not exceed 4.0 mg for the water absorption bulb and 0.3 mg for the carbon dioxide absorption bulb. If either blank exceeds this maximum, repeat the blank determination.
13. Determine the blanks at the beginning of each day the train is to be operated.

Procedure

1. While weighing the absorption bulbs from the previous run, cool the first furnace and adjust the Variac to about one half the 800° C setting.
2. Weigh a 0.5-g portion of the sample into a boat. Cover sample with 3 g copper oxide and place a cover on the boat.
3. Reconnect and open the absorption bulbs.
4. Remove the stopper from the combustion tube and insert the covered boat containing the sample into the hot zone of the first furnace.
5. Close the cover of the furnace and adjust the Variac to the 800° C setting.
6. Allow to combust for 50 minutes.
7. Remove and close the water and carbon dioxide absorption bulbs.
8. Remove the spent boat from the combustion tube.
9. Weigh the adsorption bulbs against the prepared counterweights.
10. The increase in weights of the water and carbon dioxide absorption bulbs represent the weights of water and carbon dioxide, respectively.

Calculations

1. Hydrogen:

$$\text{percent H} = \frac{(\text{H}_2\text{O weight} - \text{blank}) \times 0.1119 \times 100}{\text{Sample Weight}}$$

2. Carbon:

$$\text{percent C} = \frac{\text{CO}_2^* \text{ weight} \times 0.2729 \times 100}{\text{Sample Weight}}$$

* A blank of 0.3 mg or less may be disregarded.

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