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Project Summary

Land Treatment of Petroleum Refinery Sludges

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The purpose of this study was to identify, evaluate and optimize the factors which influence land treatment of oily residues. A research site owned by the University of Oklahoma was used. A total of 45, 6.1 m x 2.7 m (6 ft x 9 ft), plots were prepared and API Separator sludge was applied to the plots at loading rates between 3 and 13 weight percent per year, and loading frequencies from 1 to 12 times per year. The soil was analyzed for oil content, selected heavy metals, selected organic priority pollutants, pH, nitrate, and chloride over an 18-month period. Oxygen levels in the soil atmosphere, and the emission rate of volatile hydrocarbons were monitored. A laboratory study to identify and quantify volatile hydrocarbons emited also was performed. Fractionation analysis of sludges and recovered oils were done for saturates, aromatics and polar compounds and asphaltenes.

Total oil losses were proportional to the amount of oil applied with mean losses over the study period equal to 54 percent of the oil applied. Losses of the saturates fraction were highest followed by aromatics, polar compounds, and asphaltenes. Volatile losses as a percentage of the oil applied were relatively small over the long term, but were substantial in terms of short-term losses immediately after application. Biodegradation of both total oil and individual oil fractions followed first-order reaction kinetics. A composite first-order biodegradation rate coefficient of 0.003 day^{-1} was computed after compensation for volatilization.

Site monitoring determined that heavy metals were immobilized and the organic priority pollutants were degraded in the zone of incorporation (top 30 cm). Some buildup of metals occurred over the study period.

Operational considerations such as sludge loading rates and frequencies, proper tillage of the zone of incorporation, prevention of oil percolation and runoff, and operation of field equipment after sludge application are important factors in the design of land treatment facilities.

The full report was submitted in fulfillment of Cooperative Agreement No. CR80757810 by the School of Civil Engineering and Environmental Science, University of Oklahoma under the sponsorship of the U.S. Environmental Protection Agency. The report covers a project period from April, 1980 to April, 1983; field and lab work was completed in June 1983.

This Project Summary was developed by EPA's Robert S. Kerr Environmental Research Laboratory, Ada, OK, to announce key findings of the research project that are fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The purpose of this study was to identify, evaluate and optimize the factors which influence land treatment of oily residues. A research site owned by the University of Oklahoma was used. A total of 45, 6.1 m x 2.7 m (6 ft x 9 ft), plots were prepared and API Separator sludge was applied to the plots at loading rates between 3 and 13 weight percent per year, and loading frequencies from 1 to 12 time per year. The soil was analyzed for oil content, selected heavy metals, selected organic priority pollutants, pH, nitrate, and chloride a 18-month period. Oxygen levels in the soil atmosphere, and the emission rate of volatile hydrocarbons were monitored. A laboratory study to identify and quantify volatile hydrocarbons emitted also was performed. Fractionation analysis of sludges and recovered oils were done for saturates, aromatics and polar compounds and asphaltenes.

The major objectives of the study are as follows:

(1) Determine the design criteria for the land teatment process as it applies to oily residues. The criteria are loading rates and application frequences and tilling frequency.
(2) Study the fate of selected priority pollutants commonly present in oily residues.
(3) Assess the atmospheric emissions from land treatment application of oily residues.

A sampling program was established so rates of degradation could be determined. The soil in the zone of incorporation, top 30.0 cm (11.8 in.) of the research plots was sampled periodically for oil content, pH, moisture content, and nutrients. A 4 x 4 factorial experiment was proposed with loading rate and loading frequency as the two variables. Duplicate combinations of loading rates and frequencies were established. The experimental design, including loading rates and frequencies, were modified as the study progressed. Limited oil content monitoring from the unsaturated zone of heavily loaded plots was performed to determine the extent of migration of oil below the zone of incorporation.

The fate of selected organic and inorganic priority pollutants was determined on two plots with moderate loading rates. Samples were collected from the top 30.0 cm (11.8 in.) for priority pollutant analyses. Samples were also taken below the zone of incorporation to determine if priority pollutants were migrating.

Atmospheric emissions from land treatment were also assessed. The objectives were: 1) to determine the rate and magnitude of fugitive hydrocarbon emissions from land treatment of refinery sludges, 2) to identify the relative effects of such parameters as sludge loading rate, temperature, soil moisture content and relative humidity on the magnitude of hydrocarbon emissions, 3) to identify and quantify individual compounds being emitted to the atmosphere, and 4) to develop a statistical model to predict the total volatile emissions rate based on the above mentioned variables.

Fractionation studies were conducted on two moderately loaded plots to investigate the loss kinetics of individual oil fractions. A fractionation scheme separated the recovered hydrocarbons into four fractions: saturates, asphaltenes, aromatics, and polar compounds.

Results and Discussion

Oil Loss Rates

The oil content of the site soil was monitored over the study period to determine oil degradation/loss rates. Table 1 presents the total losses for the two-year project period. The oil content was calculated on a percent dry weight basis (% dwb). There was good correlation ($R^2 = 0.91$) between total loss (% dwb) and total loading (% dwb) during the first year. The correlation coefficient for the regression of total second year losses on second year loadings was 0.81. However, regression of total losses on the sum of the first year's antecedent oil content and the second year's oil loading yielded a correlation coefficient of 0.94, indicating that total oil loss was a function of the sum of antecedent oil plus oil applied in the second year, and not just that applied during the second year.

The total loss data for the first year, the second year, and for the entire study period indicated that oil losses increased in proportion to the total oil loadings. An average of 54% of the total oil applied disappeared during the overall study period of 657 days with a range from 37.3% to 82.3%. This contrasted with the data presented in the first year for which the average percent of applied oil lost was equal to 39.6% with a range from 9% to 71%.

Table 1. *Total Losses During Two Year Study Period*

Plot	*Percent dwb Lost (% dwb)*	*Percent of Total Lost (%)*	*Average Percent dwb Lost Per Day (% dwb/day)*
1	9.22	46.0	0.014
2	4.02	37.3	0.007
4	2.52	60.8	0.004
5	7.89	53.0	0.012
6	11.88	59.3	0.018
7	3.59	42.1	0.005
8	6.15	63.5	0.026
9	2.44	44.5	0.004
10	7.91	53.6	0.012
11	3.96	46.4	0.006
13	4.68	50.9	0.007
14	1.62	43.3	0.002
15	6.88	46.6	0.011
16	4.92	47.5	0.008
17	5.79	67.1	0.010
18	1.39	49.9	0.002
20	8.84	46.6	0.011
21	15.69	68.8	0.024
22	13.86	61.8	0.021
23	14.24	65.7	0.023
24	3.34	44.7	0.005
25	0.88	39.8	0.001
26	6.98	58.0	0.011
28	13.40	54.2	0.020
29	12.51	55.6	0.019
30	11.68	82.3	0.018
31	6.75	78.3	0.010
32	2.64	53.7	0.004
34	4.05	49.2	0.006
35	13.46	72.9	0.020
36	5.23	41.7	0.008
38	3.37	45.1	0.005

Rate Constant Evaluation

Rates constants for the disappearance of oil from the soil were determined for periods of time immediately following application and for periods several months after application. Average first-order rate coefficients for periods immediately following application was 0.0065 with a standard deviation of 0.0046. Coefficients for time periods several weeks after application were 0.0046 and 0.0029 with standard deviations of 0.0017 and 0.0010 for the first and second year periods, respectively. The fact that coefficients are higher in periods immediately following application than during later periods suggests either some oil fractions are preferentially degraded, or loss of oil by mecanisms other than biological, possibly volatilization, occurs simultaneously with biodegradation to determine the magnitude of oil losses via volatilization, a study of volatile emission rates was performed which is discussed in the next section. The results of this study were merged with total losses to assess the impact on rate coefficients.

Rate coefficients were calculated based on total losses and on total losses minus volatilization which is considered to be predominately of biological origin. The removal of volatile losses from the total losses in the computation of the rate coefficients had the effect of decreasing the variance as well as lowering the mean coefficient from 0.0057 to 0.0033. It is interesting to note that the 0.0033 value closely approximates the mean value of 0.0046 and 0.0029 for the first and second year, respectively, over a period several weeks after application and the 0.0057 value correspond the value 0.0065 over a short period immediately following application. Therefore, the differences in the coefficients determined from data taken immediately after application and those determined weeks after application can be attributed to the loss of volatile organics.

Volatile Emissions from Land Treatment of Petroleum Residues

The volatile emissions from land treatment of petroleum sludge were assessed in this study. Both laboratory and field studies were used in this assessment. The laboratory tests were used to measure the volatility of the sludge, and to estimate weight loss of individual sludge components as a function of loading rates, soil temperature, relative humidity, and soil moisture. Total volatile losses were also evaluated in the field, and compared with laboratory results.

The results of the laboratory tests show that a very sharp rise in the hydrocarbon concentration in the air appeared during and immediately following sludge application. An abrupt decline from the maximum concentration through a gradual transition to a lower concentration followed. The hydrocarbon concentration in most tests dropped to less than 50 percent of its maximum value within two hours after application. The laboratory experiments revealed facts that emission rates increased with increases in loading rates, temperature and soil moisture and decreased with increasing humidity.

The field data showed that higher loading rates resulted in higher volatile losses, assuming all other conditions were constant. It was also found that there was a variation in the amount of volatile losses, at a given loading rate, from one application to another. This variation could be explained primarily on the basis of volatility of different batches of sludges. It was found that volatility of the sludge was a very important factor in determining emission rates. For this reason a stripping test was developed in an attempt to provide a quantitative measure of relative volatility which could be related to emission rates.

Two models were developed using laboratory data relating emission rate in (g/hr) to loading rate, soil temperature, soil moisture, relative humidity and time since application. The first model was developed for the 10-hour time period immediately following application, and the second for greater than 10 hours. The models are presented below:

Model I - Time < 10 hours

$$Y = 76.594 + 9.985X_1 .769X_2 + 8.828X_3 - 2.025X_4 - 20.645X_5$$

Model II - Time > 10 hours

$$Y = .184 + .931X_1 + .268X_2 + 1.879X_3 - .371X_4 - .084X_5$$

Y = emission rate (g/hr)

X_1 = percent loading rate

X_2 = soil temperature (°F)
X_3 = soil moisture content (%)
X_4 = relative humidity (%)
X_5 = time since application (hr).

Applying these models to field data, resulted in a high correlation between the field results and model predictions. Using concentrations of hydrocarbons predicted by the above models in the box model for calculating equilibrium concentrations of air pollutants, the ambient concentration of hydrocarbons worst case conditions was found to be below the Oklahoma Ambient Air Quality Standards.

Fractionation Studies

Oil recovered from sampling two moderately loaded plots was fractionated and the weight fractions determined for saturates, aromatics, polar compounds and asphaltenes. Several samples from the plots were analyzed over the two-year project period to determine the fate of the different oil fractions.

The highest total loss during the first period for both plots occurred for saturates, followed by aromatics, polar compounds and asphaltenes. First period losses as a percentage of the total applied were highest for saturates followed by aromatics, asphaltenes, and polar compounds.

Second period losses were found to differ substantially from those of the first period. The most surprising difference was the decrease in the losses of the saturates fraction. All fractions with the exception of polar compounds showed lower losses during the second period than the first. The relative magnitude of the individual fraction losses were highest for aromatics followed by polar compounds, asphaltenes and saturates. Losses of polar compounds increased for both plots during the second period. The second period was only approximately 170 days consisting of approximately four months of relative dormancy during which time cold weather and saturated conditions were responsible for low overall oil losses. The composition of the sludge applied at the beginning of the second period was also different than that applied during the first period. The weight fraction of saturates was less than half and all of the other fractions were from 33 to 295 percent higher than for sludges applied during the first period.

Anomalous increases in concentration of asphaltenes (pentane insoluble compounds, saturates, and polar compounds) were found following the third application of sludge. Although these increases were not expected they can be explained and have been noted by other researchers. The time period during which the increases occurred, coincided with cold weather and saturated soil conditions. Therefore, anoxic conditions existed with a possibility of anaerobic decomposition.

During the time period when an increase in polar compounds was seen, phenol, 2 nitrophenol and pentachorophenol, as well as benzene, nitrobenzene, and isophorone, were detected in the soil matrix. The relatively low apparent losses of polar compounds may be due to the production of these compounds as byproducts of the degradation of saturates and other compounds as has been suggested by several researchers. Thus, the loss rates as recorded in Table 2 only reflect the apparent net losses. Rate coefficients were highest for asphaltenes followed by saturates, polar compounds and aromatics.

Unsaturated Zone Monitoring

The results of the oil content analysis show no significant migration below the zone of incorporation. Analysis of the unsaturated zone at the end of 406 days shows that oil content values below 40 cm were similar to the background oil levels.

Table 2. *First-Order Rate Constants for Oil Fractions*

		Rate Constants (day^{-1})			
Plot	*Period*	*Asphaltenes*	*Saturates*	*Aromatics*	*Polar*
30	1	0.0310	0.0170	0.0059	—
30	2	0.0160	0.0114	0.0097	0.0130
35	1	0.0260	0.0140	0.0040	0.0055
35	2	0.0110	0.0104	0.0086	0.0104

Fate of Metals in Soil

As part of the evaluation of land treatment, the concentration of metals in the soil was monitored periodically. The concentration of selected metals in the site soil before application of any residues was determined and compared to the concentration of the same metals in the soil at different times during the project.

No significant buildup of metals occurred during the project period. Zinc and chromium were present at levels significantly above background, but the absolute values were still very low. If the metal concentrations in the plot with the highest loading rate are considered, the useful life of the plot would be limited by the zinc and cadmium concentrations. The cadmium concentration in the soil would reach the critical level in 24 years, and the zinc concentration in 17 years. No significant metal migration below the zone of incorporation occurred.

Modeling and Design of Land Treatment Systems

Several recommendations relevant to process modeling and design were made based on data presented. Although overall oil losses increase with increasing loading rates and decreasing loading frequencies, there is a practical limit above which operational consideration such as ability to operate cultivation equipment and control runoff became limiting factors.

A maximum hydraulic loading for this research site based on existing field conditions was found to be approximately 40 l/m^2 (1 gal/ft^2). At the oil concentrations of the sludges used in this study (60 - 90 percent) the maximum hydraulic loading corresponds to approximately 7 percent increase in oil concentration in a 30-cm depth zone of incorporation. Though higher loadings were in fact made, operational problems inevitably resulted.

It must be noted that the duration of the study period was not long enough for the systems to approach equilibrium. Therefore, the maximum hydraulic loading of 40 l/m^2 per application will probably not be attainable when the oil content increases as the system approaches equilibrium. Depending upon the final equilibrium concentration and the oil concentration of the sludge, a hydraulic loading to achieve an oil content per application of 3 - 4 percent is an achievable goal. Higher concentrations can be achieved by increasing the number of applications.

Oily waste land treatment systems should be designed for equilibrium conditions'. Equilibrium conditions are reached when the amount of degradable material applied is removed (via degradation and volatilization) in the period prior to the next application. During and after equilibration, the possible buildup of refractory organics and inorganics which may be produced in the process or may be present in the waste sludge must be monitored. The buildup of refractory compounds was not found to be a significant problem in the study; however, equilibrium conditions were not achieved.

Though it was shown that the various oily fractions are removed from the zone of incorporation at different rates, the metabolic pathways and biochemical interrelationships are not sufficiently understood to warrant the use of a multiple-substrate process model. Thus, a pseudo first-order single-substrate model was developed to predict time to equilibrium. Application rate and frequency were held constant. If, at equilibrium, the amount of substrate added, L_a, is equal to the amount degraded, $(L_o - L_t)$, then the following first-order relationships are valid:

$$L_t = L_o e^{-Kt}$$

$$L_a = L_o - L_t$$

$$= L_o - L_o e^{-Kt}$$

$$= L_o (1 - e^{Kt})$$

And therefore,

$$L_o = \frac{L_a}{(1 - e^{-Kt})}$$

is an expression for the maximum equilibrium concentration, where t is the (constant) time between applications of L_a. With L_o known, the number of cycles n required to reach equilibrium may be found from the equation:

$$L_o = L_a \sum_{i=o}^{n} e^{-Kti}$$

Table 3 presents a matrix of equilibrium values for combinations of loading rate and loading frequency (LR/LF) which bracket anticipated practical loading posibilities. A value of first-order rate coefficient of 0.003 day^{-1} was used in the calculations. Equilibrium was reached when an increase in maximum concentration was less than 1 percent of the previous maximum. Based on the above assumptions the system would reach equilibrium in four to five years.

Conclusions and Recommendations

Conclusions

1. The project demonstrated that land treatment is a viable method for treatment of API separator sludge.
2. Annual loading rates should be based on projected equilibrium oil concentrations not exceeding 12 percent oil with an individual application maximum of 4 percent oil.
3. Soil should be tilled just preceeding application and then immediately following to increase the soil sorption and holding capacity, respectively.
4. Proper surface slopes are important to maintain adequate drainage and control erosion.
5. Rototilling under proper moisture conditions is important. Tilling under "wet" conditions resulted in undesirable physical changes while tilling under very dry conditions was not beneficial.
6. Losses of oil by degradation followed pseudo first-order kinetics.
7. Variation between sample replicates and detection-limiting concentrations hindered monitoring the fate of priority pollutant present in the applied waste.

Table 3. *Equilibrium Values Assuming K = .003 Day^{-1}*

LR/LF (%dwb)/(year^{-1})	L_a (%dwb)	e^{-Kt}	$L_o max$ (dwb)	L_t eq (%dwb)	n	t_2% (days)
12/1	12	.334	18.02	6.02	5	730
12/2	6	.578	14.22	8.22	9	650
12/4	3	.761	12.55	9.55	17	610
12/6	2	.833	11.98	9.98	25	600
12/12	1	.913	11.49	10.49	47	580
9/1	9	.334	13.51	4.51	4	640
9/2	4.5	.578	10.66	6.16	8	560
9/4	2.25	.761	9.41	7.16	16	520
9/6	1.5	.833	8.98	7.48	24	500
6/1	6	.334	9.01	3.01	4	500
6/1	3	.578	7.11	4.11	8	420
6/4	1.5	.761	6.27	4.77	15	380
6/6	1	.833	5.00	4.99	23	370

8. Volatile emissions accounted for about 2/3 of the losses at application, but only approximately 6 percent of the total losses over a period of several months.

Hydrocarbon emissions did not exceed 1979 National Air Quality Standards.

Recommendations

1. Further studies to reinforce the project's findings should include optimization of tillage methods under variable soil moisture conditions and soil types.
2. The influence of climate variability of waste constituents in petroleum refinery sludges, potential for air pollution, long-term effects of waste application, closed site revegetation, and monitoring requirements are areas needing further research.
3. Full-scale studies to determine waste generation, waste characteristics, storage, and land requirements are recommended.

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***Don H. Kampbell** is the EPA Project Officer (see below).*

The complete report, entitled "Land Treatment of Petroleum Refinery Sludges," (Order No. PB 85-148 708/AS; Cost: $26.50, subject to change) will be available only from:

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