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LAND TREATMENT OF OIL REFINERY SLUDGES: CHARACTERIZATION OF SELECTED ORGANICS

The University of Oklahoma PH.D. 1984

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THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

LAND TREATMENT OF OIL REFINERY SLUDGES: CHARACTERIZATION OF SELECTED ORGANICS

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

By

KESAVALU M. BAGAWANDOSS

Norman, Oklahoma

1984

LAND TREATMENT OF OIL REFINERY SLUDGES:

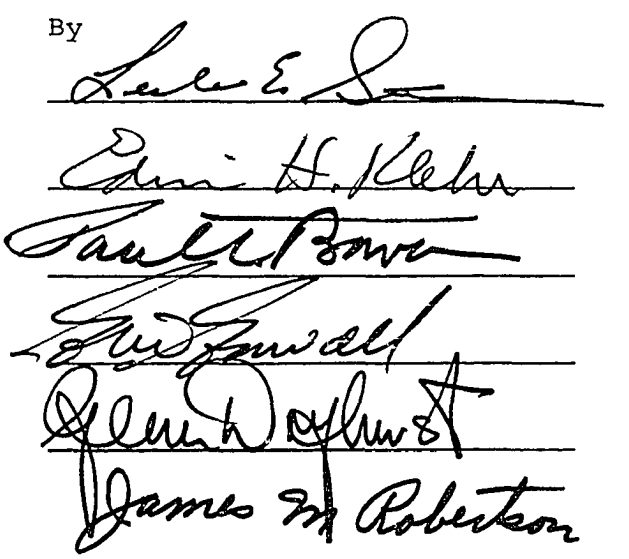
CHARACTERIZATION OF SELECTED ORGANICS

A DISSERTATION

APPROVED FOR THE DEPARTMENT OF

CIVIL ENGINEERING AND ENVIRONMENTAL SCIENCE

By



ABSTRACT

The objectives of this study were to develop an identification and quantification technique, the IQ program, for the analysis of priority pollutants; study the fate of priority pollutants present in oil refinery sludges; develop methods for sampling, sample preparation and analysis of oil content; and study the disappearance of oil fractions. The above study was performed using a ten acre tract of land owned by the University of Oklahoma.

A computer program was written for the IQ program. The IQ program followed the criteria established by the EPA. The developed program was compared with that of McLaffertys and Biemanns methods of identification and quantification. The IQ method was found to be faster than, and as reliable as, McLafferty's and Biemann's methods.

The above IQ program was used to characterize priority pollutants in the fate study. This priority pollutants study showed that pollutants degraded with time. Also, pollutants were formed in the soil matrix. Analyses of the concentrations showed variations due to the

method of analysis as well as actual variations across the plot. No significant migration of priority pollutants was detected in the unsaturated zone.

Sampling, sample preparation and analysis methods developed for the measurement of oil content yielded consistent results. The developed method was used to study the degradation of oil with time. The loss of oil ranged from 45 to 81% per year. First order empirical reaction rate constants were computed for the degradation of oil. The average rate constant was found to be 0.0088 day^{-1}. Fractionation of oil showed that all four fractions, asphaltenes, saturates, aromatics and polar compounds were degraded over time. Losses of fractions and first order rate constants were computed. No significant migration of oil was detected in the unsaturated zone.

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CHAPTER 1

INTRODUCTION

Petroleum refineries are among the top ten industrial waste generators, and the industry is among the fastest growing in the nation. Reports (1) show that 9% of refinery sludges were disposed of by land treatment in 1973 with an increase to 34% projected by 1983. Most work completed to date shows land treatment of petroleum refinery residues to be effective and environmentally safe.

Petroleum oil refinery residues typically consists of API separator sludges, slop oils, tank bottoms, dissolved air flotation sludges and refinery waste waters. The residues generally contain oil, metals and several organic components, some of which have been identified as priority pollutants. Oil refinery wastes are also a listed RCRA hazardous waste.

An extensive literature review of the land treatment of petroleum refinery wastes was performed. Of the papers reviewed, data were found for no more than 7 different land treatment operations. In general, information exists concerning site selection, site preparation,

runoff control, potential migration of constituents and methods of sludge application. However, many questions relative to the loading rates, loading frequencies, optimization of the process, and design life and closure still exist. Questions also exist concerning the rate of degradation of priority pollutants and degradation of oil and its individual fractions.

The objectives of this research effort are: study of the degradation of the organic refinery waste components in the land treatment process by monitoring gross oil content and the ASTM D2007 oil fraction parameters in the waste and soil matrix - examining the fate of priority pollutants present in oil refinery wastes applied to the land treatment system. The present study is a part of the land treatment study performed at the University of Oklahoma funded by the U.S. EPA.

CHAPTER 2

LITERATURE REVIEW

LAND TREATMENT OF OILY RESIDUES

Land treatment of oily sludges has been in practice for many years. Recently, more and more oily wastes have been disposed on land. Most of the literature focuses on the design of land treatment systems and disappearance of oily sludges and fractions (asphaltenes, saturates, aromatics and polar compounds). There is very little information on the priority pollutants present in oil refinery wastes.

Huddleston and Cresswell (1976) reported two different studies on the application of oily wastes to land. At Billings, Montana, they found an oil loss of 7.2 g/kg of soil over a period of 18 months. They believe the loss was due to loss of individual fractions of oil, aromatics, paraffins and resin-asphaltenes. The waste initially consisted of 50% paraffins, 30% aromatics and 20% resin asphaltenes. At the end of 18 months, only 20% paraffins and 15% aromatics remained of the original amount while the resin-asphaltenes fraction had increased to 65%. In their Ponca City site there was a loss of 3.6

hg/kg of soil over a period of 24 months. At the end of 22 months 80% of the resin-asphaltenes remained.

Kincannon (1972) studied the rate of oil decomposition by the application of residues from tank bottoms on land. The rate of decomposition was found to be slow during winter months and also when the oil concentration exceeded 10% by weight. He also reported that aromatics and saturated hydrocarbons were reduced in the soil over a period of time.

Watts et al., (1981) studied the land application of industrial oils and solvents. No noticeable migration of the oils into the soil profile was found. There was loss of oil at a rate of 20,000 kg/ha/year. One year after the initial application, the CO_2 emission rate was found to be six times greater on plots which had oil applied than on control sites without oil. The authors also reported that oil biodegradation was not affected by fertilizer levels.

Raymond et al., (1976) studied degradation of six different oils (crank case oil from cans, crank case oils from trucks, Arabian heavy crude oil, coastal mix crude oil, home heating oil no. 2 and residual fuel oil no. 6) at three different locations: Marcus Hook, Pennsylvania, Tulsa, Oklahoma and Corpus Christi, Texas. The application rate was 11.9 m^3 $4x10^3$ m^2. Half of the plots at every location were fertilized and the other half were

not. The average oil loss reported ranged from 48.5 to 90% per year and varied with the type of oil and the location of the site. The paraffinic (heavy fractions, not saturates) rate of degradation was very slow, and significant amounts of paraffinic material remained after one year at all three locations. Results of their fertilizer study showed minimal effects of fertilizer application. The researchers encountered problems in the lack of homogeneity of the soil matrix, and a recommendation was made for tilling more frequently.

Walker et al., (1976) studied the biodegradation rates of petroleum using South Louisiana Crude Oil. Computerized mass spectrometry was used to monitor changes in saturates, aromatics, resins and asphaltenes over time. Saturates were the only components which showed a steady decrease. Aromatics were found to decrease during the first week, remain constant from week 2-3 and increase during weeks 3-7. Resins and asphaltenes were found to increase with time.

Myers and Huddleston (1979) reported a substantial increase in land treatment efficiency at moderate loading rates of fertilizer compared to both high and low loading rates. The low loading rate was 1:800 TOC:N, and the high loading rate was 1:400 of TOC:N. The moderate loading rate was not defined. However, the major factor which affected the loss of oil was tilling. The loading

rate of oil was 5% by weight of oil per year. Vegetative cover slowed the rate of degradation by about 30%. There was no leaching of oil.

Dibble and Bartha (1979) conducted a laboratory study on the leaching aspects of oily sludges in the soil matrix. The soil used for the study contained 42% sand, 34% silt, and 25% clay. Oily sludge was incorporated into the soil matrix at a rate of 30 g hydrocarbon/600 g of soil. Nutrients were added in ratios of C:N 200:1 and C:P:K of 26:40:111. Nitrogen was added as urea (46.7-0-0), urea paraffin (26.8-0-0) and urea formaldehyde (38-0-0). Phosphorus was added as octylphosphate (0-26-0) or triple super phosphate (0-44-0) and potassium as KCL (0-0-60). The highest sludge biodegradation rate in the soil matrix was 1.2 g hydrocarbon/100 g soil/120 days. Increases in TOC were observed in the leachates. There was no significant migration of hydrocarbons.

Microbiological degradation of organic acids was studied by Rogers et al., (1981). This was a laboratory study using liquid cultures inoculated into the soil. Organic acids identified in these waters were mono and dicarboxyllic and benzoic acids. Acids in solution were reduced by 80 to 90 percent with 9 days incubation. From mass balance calculations, the decreases in dissolved organic carbon over the time of incubation was found to equal the formation of CO_2 and bacterial cell carbon.

Jobson et al., (1972) studied microbial utilization of two different crude oils using bacterial cultures. Studies were performed in the laboratory at 4 and 30° C. One oil was of higher quality (North Cantal oil) than the other (Lost Horse Hill crude oil). North Cantal oil utilization was found to be significant at 30° C. Specific gravity of North Cantal oil changed from 0.827 to 1.046 over a period of time. The Lost Horse Hill crude oil did not change in specific gravity. This was probably due to the absence of saturates since preferential utilization of saturates was observed.

Jobson et al., (1979) conducted a field study for a period of 308 days using bacterial cultures, fertilizer application and replicate plots. The application of fertilizer increased the utilization rate of the n-saturate fraction and the bacterial count. The application of fertilizer had a direct effect on all other factors.

Westlake et al., (1978) investigated the rate of degradation of oil in a soil of the Boreal region of the Northwest Territories. Fertilizer and bacteria were applied with oil. In fertilizer applied plots, there was a rapid increase in bacterial count. The saturates content of the fertilizer applied plots decreased with time. Treatment of plots with oil degrading bacteria did not accelerate the rate at which chemical changes in recovered oil occurred. The reason given for this phenome-

non was that the presence of indigenous oil degrading bacteria in those soils was high compared to the amount of bacteria introduced.

Stanlake and Finn (1982) isolated and characterized the bacteria which degrade pentachlorophenols (PCP) and 2,4,6-trichlorophenols. They isolated the genus Arthrobacter as the phenol degrading bacteria. The degradation of the phenols commenced after a lag of 1 to 2 weeks. However, no correlation of degradation with the extent of bacterial growth was obtained. Initially, the degradation took 1 to 2 weeks. Further loadings were found to degrade in 1 to 3 days.

Rosazza (1982) reviewed the work of several authors (Liu et al., 1977; Chin et al., 1970) and compared them to his own work on the microbial transformations of organic compounds to asphaltenes. The enzymatic and non-enzymatic processes synthesized anilines, aromatic compounds and phenols into quinolines, sulfoxides, carbazoles, pyridines and amides, which represent the polar compounds.

Okinsky and Umbreit (1959) studied the anaerobic decomposition of aromatic compounds. They found that carboxylic acids, aldehydes, hydrocarbons, ketones and esters were intermediate products of anaerobic decomposition. The same phenomenon was observed by Waksman (1927) and Evans (1977).

Evans (1977) delineated the anaerobic dissimilation of the benzene nucleus under three different sets of biological conditions. The three conditions were: anaerobic photometabolism of benzoate by the Athiorhodaceae, anaerobic metabolism of benzoate through nitrate respiration, and methanogenic fermentation by a consortium. All the above mechanisms yielded intermediate compounds such as carboxylic acids, phenols, esters, ketones, alcohols, aldehydes and hydrocarbons.

Parekh et al., (1977) observed that aliphatic hydrocarbons degraded anaerobically via nitrate respiration to produce pentane insoluble compounds. The pentane insoluble compounds are classified as asphaltenes in a later chapter of this study.

IDENTIFICATION AND QUANTIFICATION TECHNIQUES IN GC/MS/DS

Interfacing of computers with analytical instrumentation has greatly accelerated and simplified data acquisition and interpretation. Hites and Biemann (1967) were the first to develop a method of recording mass spectra in digital form; this introduced the flexibility of further manipulation of the spectral data. Compilation of large spectral libraries was made possible at reasonable costs. Subsequently, they coupled their new data acquisition system with a gas chromatograph and collected both the mass spectrum and the chromatogram simultaneously.

Several researchers (3,4,16,17,18,19,20,21,22) have developed computer programs for the quantification and identification of organic compounds. However, none of the above programs follow EPA protocols. The commercial programs available (FINNIGAN - MAT) are a blend of McLafferty's and Biemann's methods. Therefore, this literature review section contains those two works, since the other programs are not pertinent to the present study.

Commercial programs were not available within the existing GC/MS/DS system. Most commercial methods of identification and quantification are probability-based matching methods; this means that even if there is only a partial spectrum available for a compound, it could be positively identified as a certain compound, even though it is not actually the compound (false positive). Even though false positives occur in the real-world analysis of samples, no literature exists dealing with this problem. Recently, Bruce Colby (1984) presented a paper in a conference in Virginia criticizing McLafferty's method; however, no data were presented.

McLafferty et al., (1974) developed a computer algorithm for rapid identification of specific compounds in mixtures called the "Probability Based Matching System" (PBM). A confidence Index "K" was established based on the probability of a specific compound being present.

The system described consists of a reverse search, in which the question, "Is this mass spectrum caused by R?" (where R is a compound) was asked.

Derivation of the Confidence Index was based on three factors which were assumed to be independent. The total probability was the product of all individual probabilities. The K value was the summation of the individual values K_j, found for each peak examined. K_j was assumed to be a linear combination of the factors. The following equation was derived relating the factors:

$$K = e\ K_j = e\ (U_j - A_j - D - W_j)$$

where U_j = uniqueness of the m/e value of the jth peak;

A_j = abundance factor based on the abundance in the reference spectrum;

D = "dilution factor", which is the correction applied for decrease abundances in a mixture of compounds;

W_j = "window tolerance" which reflects the narrowness of the peak abundance criteria used.

Uniqueness was based on the probability that abundance of the peak mass in question would be greater than 50% of the base peak of the spectrum taken at random. Fluctuations of U for m/e greater than 150 were small. For general applications of PBM a U value of 10 was recommended.

Analyses of the U values obtained for the compounds

in this study showed that 1 in 32 spectra had an abundance greater than 50% for a m/e peak of 45. For the 32 spectra nearly half of the m/e 45 peaks had an abundance of greater than 1%. In order to evaluate the uniqueness of the peak of less than 50% abundance, its U value had to be reduced. A good approximation of K was obtained from a large sampling of spectra by subtracting A from U. Confirmation of this approximation was made by agreement with the data of Grotch.

Overlapping of peaks was corrected by applying the abundance correction factor, the dilution factor D. For mixtures of compounds, a halving of the proportion of the target compound resulted in further subtraction of one from D.

Another requirement for successful identification was that the relative abundances of the peaks should be consistent with the reference spectrum. The expected degree of matching of these abundances was termed Window Tolerance, W. Only one in sixteen had an abundance falling within a 20% window of the peak selected. The effects of U, A, sample size, window tolerance and impurities were studied with drugs of abuse and structurally similar compounds. Finally, analysis of K values revealed that there was only a "one in a million" chance that the spectrum was from a molecule unrelated to the target compound.

McLafferty et al., (1976) modified the PBM system to permit matching of an unkncwn spectrum with a large data base not restricted to spectra taken under the same experimental conditions. The search algorithm matched peaks with the reference compound; if a peak was not found in the unknown then the peaks not found were flagged. If the number of missing peaks exceeded the maximum number of allowed flagged peaks, the program continued on to the next reference compound. The K value (Confidence Index) from the match was compared with the threshold K value; if the K was smaller than the threshold, the results were discarded.

To analyze the data obtained, recall reliability values were computed. The retrieval system was tested using two sets of compounds, a low molecular weight set (LMWS) and a high molecular weight set (HMWS). A plot of the recall-reliability values showed that in the high reliability range (50%), the PBM performance was the same for the LMWS and for the HMWS.

Rosenthal (1982) described the possibility of misidentifications in direct search systems (Biemann). He calculated the probabilities for a 200 compound mixture and found that approximately 20% of the compounds were liable for mismatches. He concluded that other searching techniques such as reverse search (McLafferty), spectrum stripping, classification by retention time, (Biemann)

iterative processing and combined strategies should be used.

In the above methods large data systems and computers, like the IBM 370, were used. The present study consisted of using the three EPA criteria (1. all three peaks must be present; 2. the peaks should be within 20% of the standard peaks; 3. the retention time of the peak should be within 60 secs. of the standard peak) for peak matching. A HP21MXE computer with a 20 megabyte dual disk drive was used. The algorithms used in the above methods were long; this reduced the speed of analysis. McLafferty's method would identify a compound even if only a portion of the peaks were present. This method leads to inspection of spectra before acceptance of identity of a compound. The PBM, Biemann's and the other methods described above do not follow the three EPA criteria.

FATE OF PRIORITY POLLUTANTS

A summary of the probable fate of priority pollutants in water related environments has been reviewed by Micheal et al., (1979). This literature survey was supported by the EPA. The chemical properties of the priority pollutants were included. Based on the established fate of a few pollutants in water, the fate of other priority pollutants were predicted using

structural and chemical similarities.

Recently, Canviro Consultants Ltd., (1983) conducted a literature survey on the significance of trace substances in petroleum sludges disposed on land. This survey was done for the Petroleum Association for Conservation of the Canadian Environment. Analytical methods for the extraction of priority pollutants from petroleum sludges have been reviewed. The review shows that very little information exists on the characterization, quantification and fate of priority pollutants from petroleum sludges. Reference has been made to preliminary data from the present study. A better data base exists for concentrations of trace metals in refinery sludges than for trace organics. A list of researchers in the area of land disposal of petroleum sludges has been compiled by the above author.

CHAPTER 3

SCOPE OF WORK

SCOPE OF OVERALL LAND TREATMENT

The objective of the land treatment study, performed by researchers in School of Civil Engineering and Environmental Science at the University of Oklahoma, was to establish process guidelines for the treatment of oily sludges from petroleum refineries in order to answer the questions relating to the land treatment process as mentioned in Chapter 1.

The objective included:

* loading rate guidelines
* loading frequency guidelines
* tilling frequency guidelines
* determining the effect of volatile emissions due to land treatment
* characterization and treatment of priority pollutants
* unsaturated zone monitoring
* study of the degradation of oil
* study of degradation of oily fractions (asphaltenes, saturates, aromatics and polar compounds)
* development of analytical methods for the above studies

SCOPE OF THIS DISSERTATION

The two major objectives of this study were to examine the degradation of oil and its individual fractions, and to study the fate of priority pollutants in terms of their formation, disappearance and percolation in the soil. In order to fulfill the above objectives, several other studies had to be conducted. The following paragraphs will focus on the entirety of the above research.

In order to study the rate of degradation of oil and fractions, methods for sampling, sample preparation and analysis had to be developed, since the existing methods did not yield consistent results. Several methods of sampling for oil content were evaluated, and a method was chosen based upon consideration of different types of samplers and sampling methods. Simultaneously, a method for sample preparation and a method for oil content analysis were also developed. The developed method was compared with existing oil content analysis procedures. Oil losses were evaluated, and the degradation rates were computed. The problems associated with land treatment of oily residues, as well as factors affecting the treatment process, were also evaluated.

Evaluation of the fate of oily fractions was studied by dividing the oil into four fractions - asphaltenes, polar compounds, saturates and aromatics. The loss of

individual fractions and the rate coefficients were computed and compared with the total oil degradation.

The fate of priority pollutants was studied by characterizing the sludges before application and the soil matrix after application. The tool used for characterization of the samples was a HP5985B Gas Chromatograph/ Mass spectrometer equipped with 21MXE series data system (GC/MS/DS).

The GC/MS/DS used did not have the software to do library searching and quantification. Therefore, a computer program was written for identification and quantification (IQ program) following the EPA protocols.

In order to test the reliability of the IQ program, two other programs were written for McLafferty's and Biemann's methods of identification and quantification. The IQ program was compared with McLafferty's and Biemann's method and the advantages of the IQ program were evaluated. Further, variations of priority pollutants across the site and due to method of analysis were also studied. Finally, the fate of priority pollutants was evaluated.

CHAPTER 4

APPROACH TO STUDY

SITE SELECTION

A ten acre site located in the Southwest 1/4, of the Northeast 1/4, of Section 14, Township 9 North, Range 3 West, Cleveland County, Oklahoma, was selected for this study. Figure 1 shows the location of the site. The site is owned by the University of Oklahoma. The climatic conditions in this area can be described as mild winters and hot summers. The winters and springs during the period of the project were unusual, in that rainfall was much above average for the duration of the project.

The following criteria represent the major considerations in selecting the location of the research site:

* The site should be owned by the University of Oklahoma.
* The site could have no past history of oil applications.
* A long term commitment of the site for use in research must be available.
* The site should be remotely located relative to urban population.

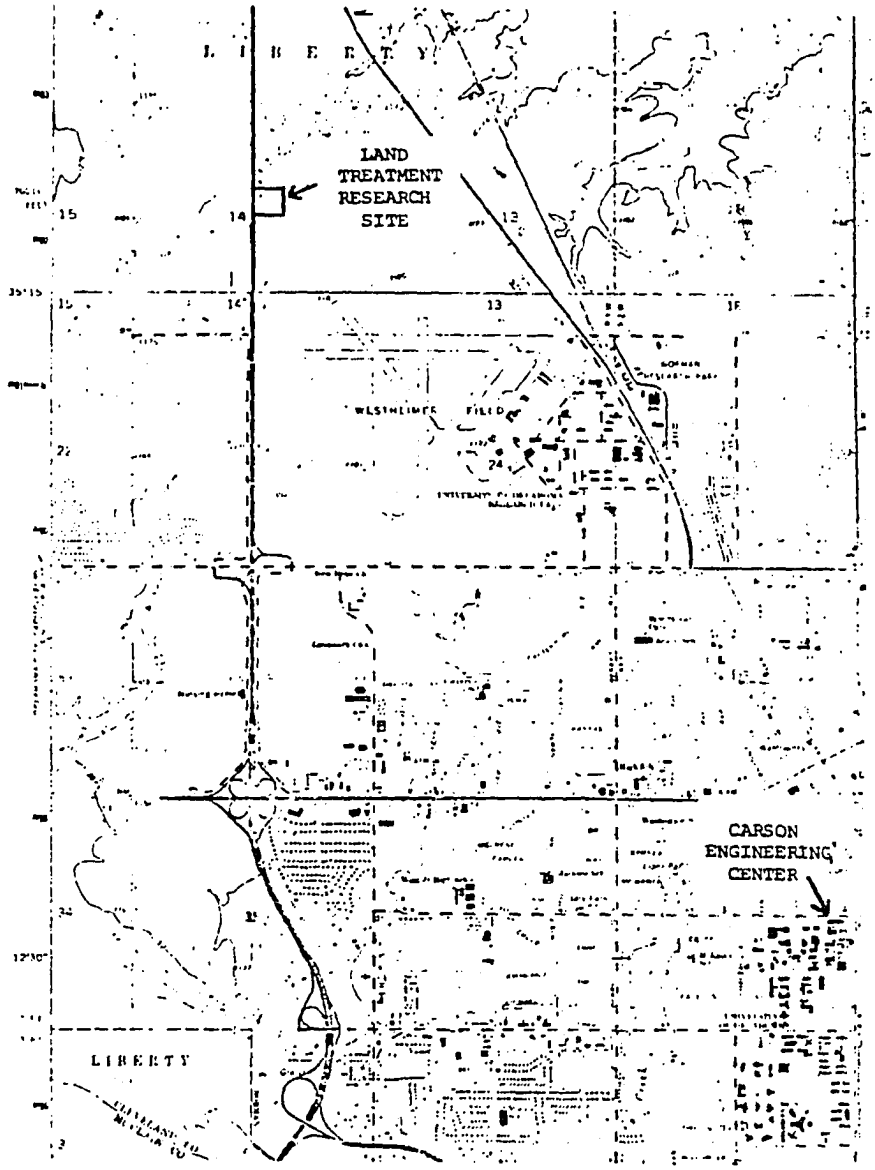


Figure 1. Land treatment research site location.

* The surface slopes should be less than 2%.
* An impermeable clay must underly the site and provide maximum vertical separation from any fresh water aquifer.
* The surface soils should represent good agricultural soils with lateral uniformity.
* Reasonable road access and economic access to water and electric utilities is needed.

The site selected could not be directly serviced with a water supply without great expense. With this exception the research site meets all of the above criteria.

SITE DESCRIPTION AND CHARACTERISTICS

The Cleveland County Soil Survey defines the surface soils at the site to be part of the Bethany Silt Loam series. A reprint of the survey description of this soil series is as follows:

Bethany silt loam, (Bb)

This dark deep noncalcareous soil of the prairies is not extensive but occupies a few fairly large areas totalling 15,200 acres northwest of Norman. Surface and internal drainage are both very slow, but the soil is adequately drained for all crops commonly grown. It has a high water holding capacity and absorbs most of the precipitation, but crops are sometimes damaged during long droughts. One reason is that plants are unable to obtain

water fast enough from the clay in the lower subsoil layers when the soil moisture content is low. Slope is less than 1%, therefore erosion is not a problem.

The surface soil, to a depth of about 15 inches, is a dark grayish-brown or dark-brown granular slightly acid silt loam that tends to crust on drying but is easily kept loose and granular under a wide range of moisture condition. The surface soil grades into the upper subsoil, a dark-brown or grayish-brown porous granular soil of slightly acid silty clay loam. This upper subsoil, 4 to 8 inches thick, is neither tight nor hard, even when extremely dry, and is easily penetrated by moisture, air and plant roots. The upper subsoil grades into a lower subsoil of brown firm blocky clay that continues with little change to depths of 40 to 50 inches. Next in profile is brown heavy noncalcareous clay mottled with yellow and reddish brown, which grades at depths of 6 to 8 ft. into alkaline to calcareous reddish silty clay or silty shale. This shale may be residuum of ancient water-laid materials.

SOIL ANALYSIS

Ten composite samples of eight (8) inches of soil from the site were collected for gradation analysis. Samples were collected in a manner so as to establish variation in gradation of surface soils across the site.

Gradation analysis were performed in accordance with AASHTO T 88-72, Standard Method for Particle Size Analysis of Soils which includes hydrometer analyses for the fine soil particles. Results of the analyses are presented in Table 1. The maximum variation found is within the limits of analysis error and indicates that the surface soil in the research area is very uniform texturally.

The samples described in Table 1 were further analyzed to determine their maximum densities at optimum moisture content and their plasticity characteristics. The "Harvard Miniature" procedure was used in the density measurements. The liquid limit test was conducted in accordance with AASHTO T 89-76, Standard Method for Determining the Liquid Limit of Soils. Plastic limit and plasticity index procedures as described in AASHTO T 90-70, Standard Method for Determining the Plastic Limit and Plasticity Index of Soils were followed. Results of these tests appear in Tables 2 and 3 below.

Uniformity of the surface soils on the site is further established by the low variation in the density and plasticity data. This soil is plastic over a small range of moisture contents (Table 3) indicative of the high silt and relatively low clay content of the surface soil.

Several shallow soil cores down to approximately five feet were taken across the site. In addition, shav-

Table 1 Gradation Analysis of Surface Site Soils

General Description of Sample Relative to the South 1/2 of Site	Sample Depth (inches)	% Sand	% Silt	% Clay	Textural Classification
1-A-East 1/2	0-8	4.5	78.0	17.5	Silty Loam
1-B-East 1/2 (1-A split)	0-8	3.7	79.3	17.0	Silty Loam
2-A-East 1/2	0-8	3.9	78.6	17.5	Silty Loam
3-A-West 1/2	0-8	4.3	77.2	18.5	Silty Loam
Average Results		4.1	78.3	17.6	Silty Loam

Table 2 Dry Density - Optimum Moisture Analysis Results

Sample Identification	Sample Depth (Inches)	Maximum Dry Density (PCF)	Optimum Moisture Content (%)
2-A	0-8	107.5	15
3-A	0-8	108.0	14
Average Results		107.7	14.5

Table 3 Plasticity Analyses

Identification	Sample Depth (Inches)	Liquid Limit (%Moisture)	Plastic Limit (%Moisture)	Plasticity Index (%Moisture)
1-A	0-8	23.0	21.5	1.5
1-B	0-8	23.7	21.0	2.7
2-A	0-8	24.1	20.0	4.1
3-A	0-8	23.9	20.8	3.1
Average Results		23.7	20.8	2.9

ings from four deep site cores air drilled to 100 ft. (30.5m) were examined. Inspection of the materials form these cores further indicated that a great deal of uniformity exists in the underlying strata beneath the site. A general description of the typical soil profile beneath the site is given in Figure 2.

The clay material underlying the silty loam on the surface was found to have a coefficient of permeability less than 10-7 cm/sec. The underlying clay gradually changes to red clay shale at approximately sixty inches. The red shale continues down to 100 ft. (30.5m) where drilling ceased. Thin lenses of sandstone (1 to 2 inches) were encountered at various positions in the shale beds. No ground water table was encountered in any of the deep core holes. Known area hydrogeology indicates the only major aquifer water table to be approximately five hundred feet (154m) deep or deeper in the vicinity of the site (25). The soil pH ranged from 6.5 - 8.5.

DESIGN AND OPERATION OF LAND TREATMENT SITE

Site Design and Construction

The site consists of 50 plots each of dimensions 9 ft. by 20 ft. (2.7m x 6.1m). Buffer zones are provided between each plot on all sides so that there is no interaction between materials applied on each plot. It is al-

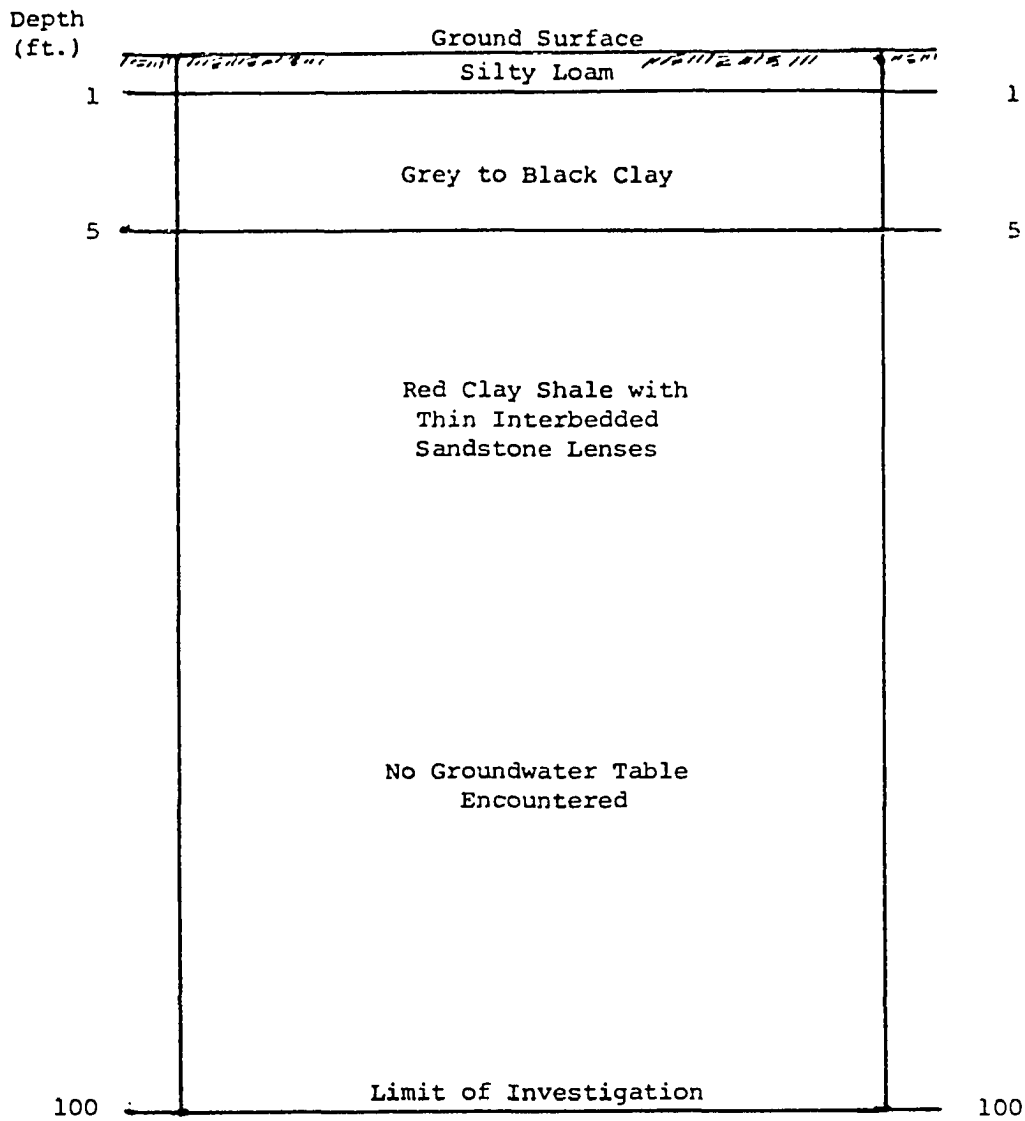


Figure 2. Typical vertical soil profile at site.

so convenient for moving the tractor and applicator around to each plot. Fifty plots were selected so that a statistically valid study could be performed.

The entire site is diked to prevent run-on and run-off of surface water. A retention pond was also constructed inside the diked area as shown in Figure 3. The retention pond was designed to retain run-off for a twenty-five-year twenty-four-hour storm. Four ground water monitoring wells were installed; one southwest, one northwest (both are upstream) one south and one northeast (both are downstream). Each well was 100 ft. deep.

The site has two storage tanks, as shown in Figure 4, with a combined capacity of 12,000 gal. to store the oil refinery sludges on site. A mixer is mounted on top of one of the tanks to provide a unfirm mixing of waste for application. The site after completion is shown in Figure 3.

Soil moisture samplers were installed in three plots at a depth of 3 ft. below the zone of incorporation. The purpose of the soil moisture samplers was to monitor the percolation of the pollutants from the sludges through the soil column.

Application of Sludges

At the land treatment research site a total of 50 test plots and 4 control plots each 6m x 2.7m (20' x 9'),

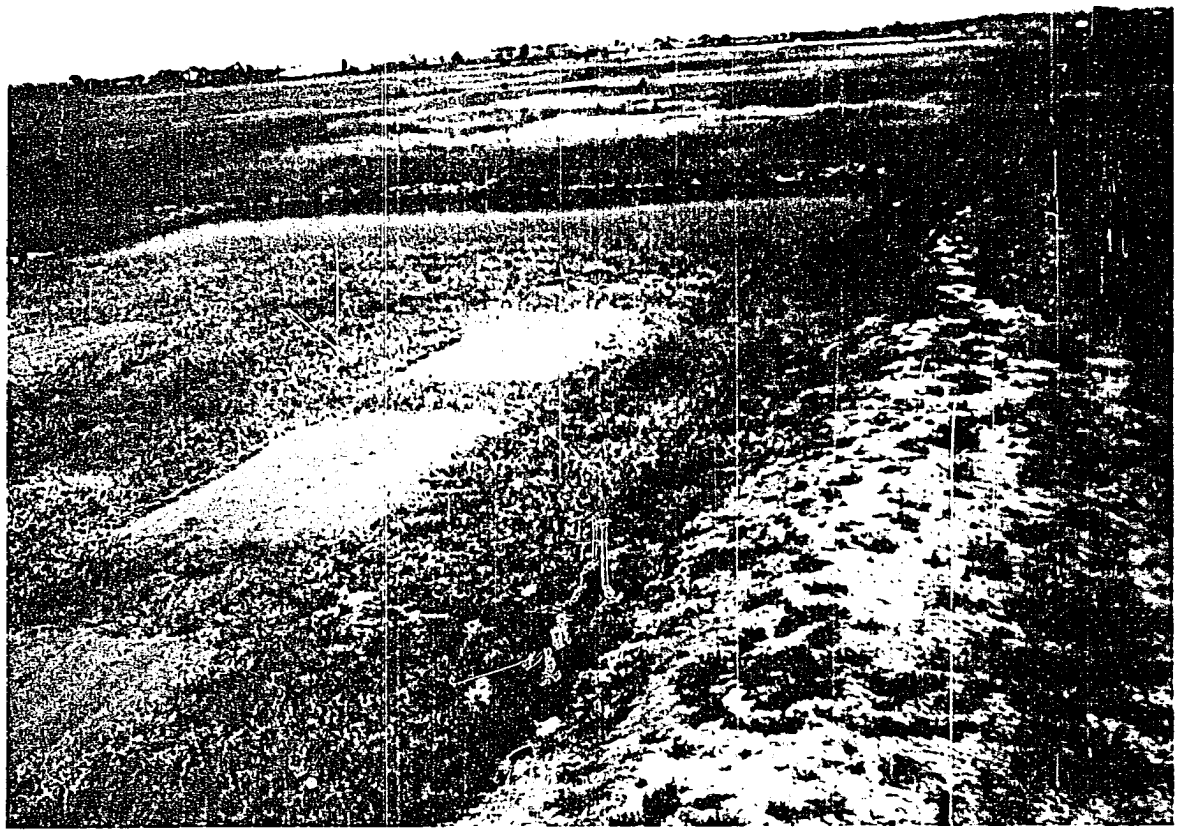


Figure 3. Completed research site.

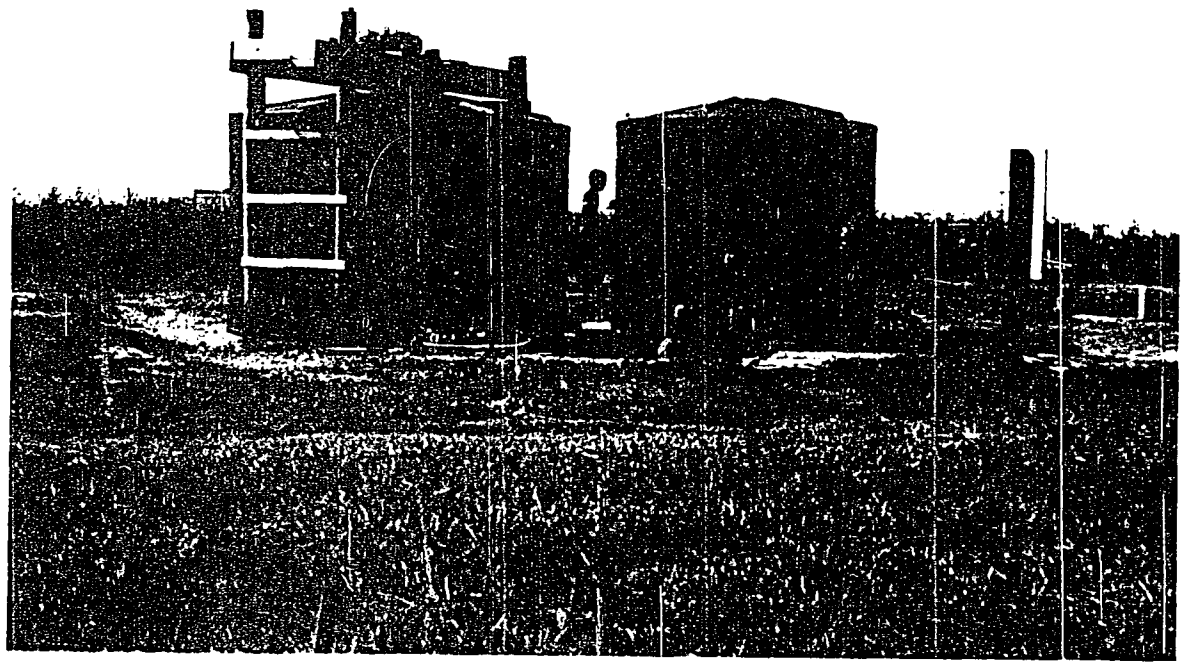


Figure 4. Site storage facility.

were established. A 4 x 4 factorial experiment was set up, with loading rate and loading frequency as the two variables. The nominal loading rates at the start of the project were 3%, 6%, 10% and 13% on a dry weight basis. The nominal loading frequencies were once, twice, six times and twelve times per year. The loading rates and frequencies were modified as discussed in the appropriate sections of the report. The loading rates and frequencies had to be modified because of several factors, including antecedent soil conditions and climatic conditions. The major factor was that over the duration of the project there was a lot of rainfall, which made oil application and tilling impossible for months at a time. A second factor was that at the higher loading rates, it was not possible to apply all the sludge at one time, because the soil became saturated and the oil would then run-off the plot. To overcome this, applications at high loading rates were spread over two days. On a number of occasions, rain intervened and the second application could not be made as scheduled, so that the loading rate and frequency for that plot was altered. All combinations of loading rates and frequencies were set up in duplicate, resulting in a total of 32 research plots (Figure 5).

Sludges were applied on the land with an applicator which has a 200 gallon tank and a 5 hp gasoline engine

1 LR = 13% FR = 6	6 LR = 13% FR = 6	11 LR = 6% FR = 6	16 LR = 6% FR = 2	21 LR = 13% FR = 2	26 LR = 13% FR = 12	31 LR = 3% FR = 2	36 LR = 13% FR = 1	41 C
2 LR = 13% FR = 12	7 LR = 6% FR = 6	12 C	17 LR = 3% FR = 2	22 LR = 10% FR = 2	27 C	32 LR = 6% FR = 12	37 C	42 LR = 13% FR = 1
3 C	8 LR = 13% FR = 2	13 LR = 10% FR = 12	18 LR = 3% FR = 12	23 LR = 13% FR = 1	28 LR = 10% FR = 1	33 C	38 LR = 3% FR = 1	43 LR = 13% FR = 1
4 LR = 3% FR = 6	9 LR = 6% FR = 12	14 LR = 3% FR = 6	19 C	24 LR = 3% FR = 1	29 LR =10% FR =1	34 LR =10% FR =12	39 C	44 LR = 10% FR = 1
5 LR = 10% FR = 6	10 LR = 6% FR = 1	15 LR = 6% FR = 1	20 LR =10% FR = 6	25 LR = 3% FR = 12	30 LR = 6% FR = 2	35 LR =10% FR = 2	40 C	45 LR = 10% FR = 1

LR = Loading Rates

FR = Frequency of Application

Figure 5. Randomized allocation of plots.

powered pump, Figure 6. The applicator consists of a manifold and a frame on which the manifold traverses. The manifold was driven by a 1/2 hp motor. The manifold consisted of six spray nozzles equally spaced to assure uniform application.

Before application, the plots were tilled and raked to obtain uniformity throughout the plot. The applicator was calibrated before each application. After application, the plots were tilled twice to ensure uniform mixing of the oily sludge in the zone of incorporation. The till zone is 12 inches deep.

Figure 7 shows the tilled plot prior to application. Figure 8 shows the appearance of the plot immediately after application. Figure 9 shows the tilling of plots and Figure 10 shows the plots after application and tilling.

PRESENT STUDY FORMAT

Fate of Priority Pollutants

This study adopted the following approach. A computer program for the identification and quantification of priority pollutants was written using the EPA protocol. The EPA criteria consisted the following conditions:

(i) The peaks for the three identifying ions must be present in a spectrum for a specified compound.

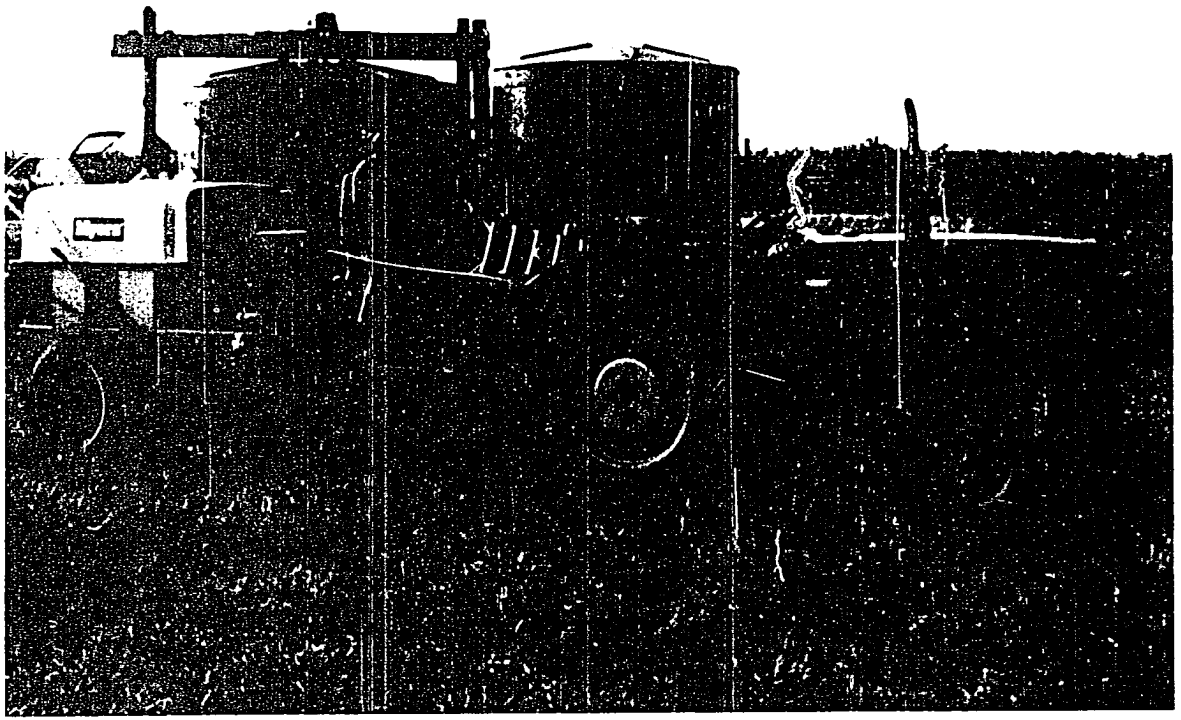


Figure 6. Residue application equipment and storage facility.

Figure 7. Tilled plot prior to application of residue.

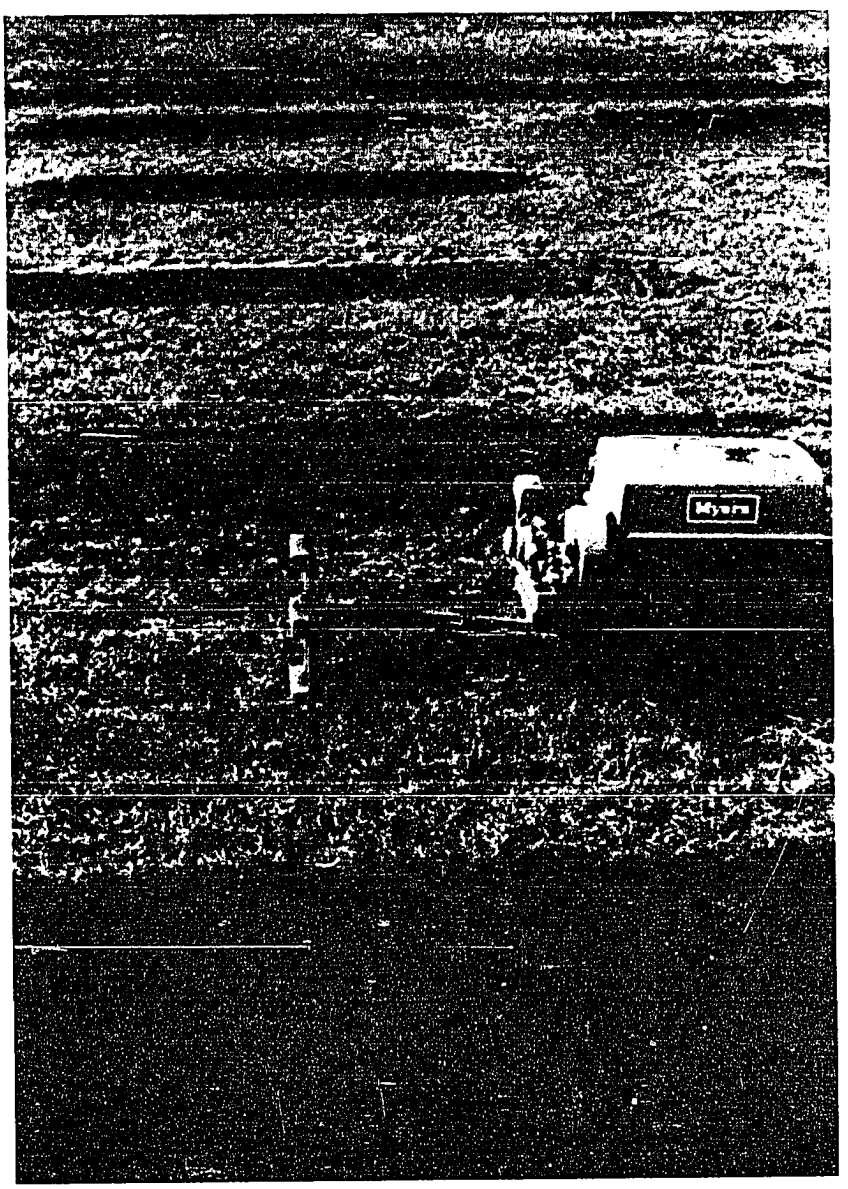


Figure 8. Plot appearance immediately after application.

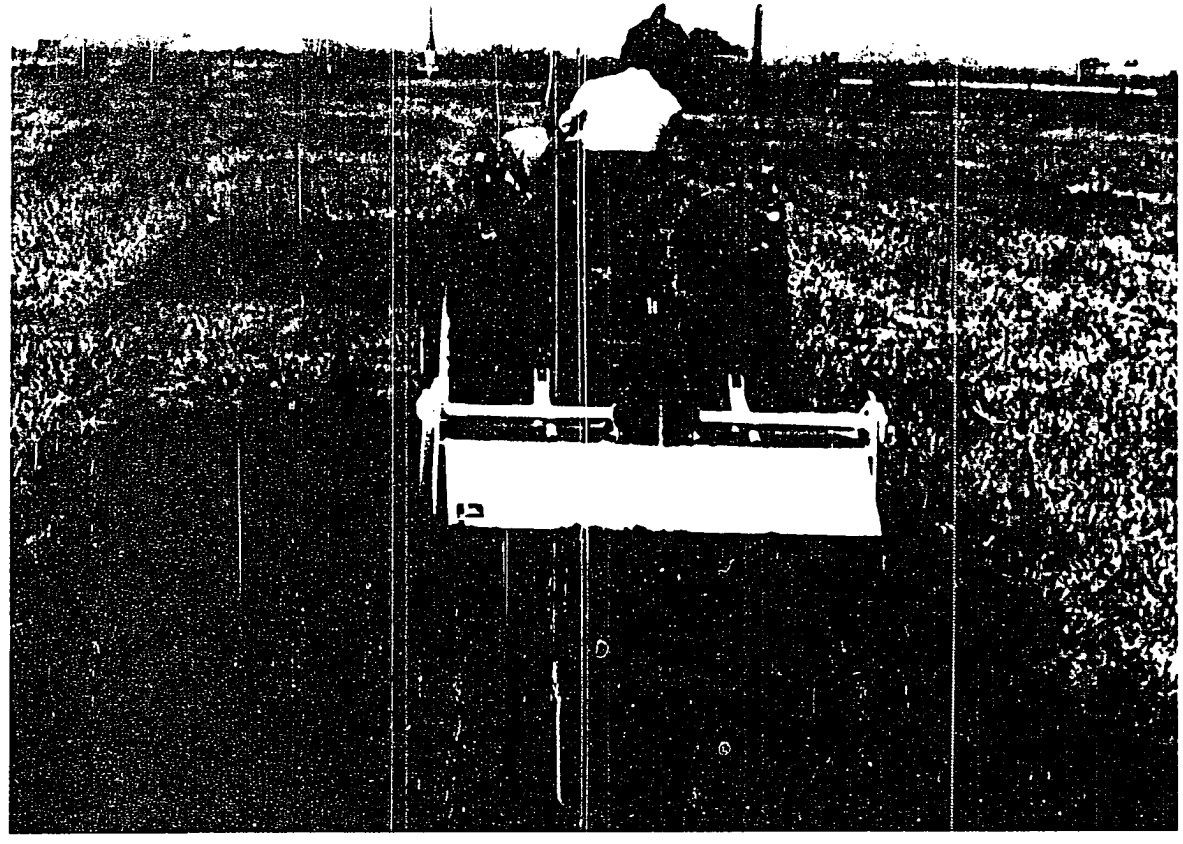


Figure 9. Plot tilling.

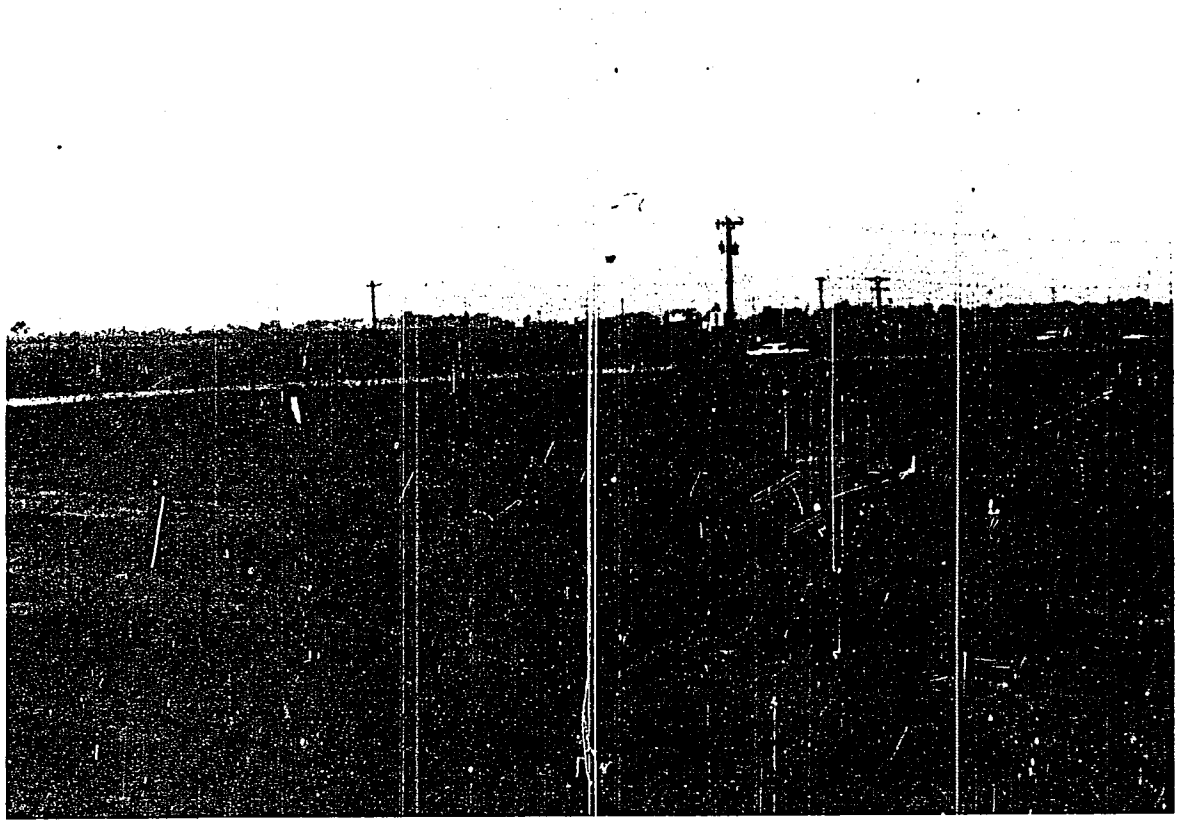


Figure 10. Plots after application and tilling.

(ii) The retention time of the identified peak must be within 1 minute of the retention time of the standard.

(iii) The spectrum of the ions for the identified peak must be within 20% of the standard in intensity. The above method was tested using seven priority pollutants over a range of retention times. The above method was compared with McLafferty's (PBMQ: Probability Based Match Method) and Hites-Biemann's Method (HIBE). Computer programs were written for the PBMQ and HIBE methods from their published works.

The fate of priority pollutants was studied using two plots each of 9 ft. x 20 ft. Nominal loading rates of these plots were 10% and 6% by weight of oil. The loading frequency was two applications per year. Only two plots were selected because of high cost of analysis and the large number of samples to be analyzed if a greater number was selected. Four samples were taken from each plot each time they were sampled. The total number of GC/MS analyses for a single plot was twelve. The reason for selecting plots with two frequencies was to allow enough time for the oily sludges to equilibrate with the soil. Heavy loading rate plots were selected to represent situations commonly occurring in industry.

Sludges and background soils were characterized before application. The soil matrix was characterized with time. Samples for the soil matrix characterization were taken from the zone of incorporation and the unsaturated zone below to follow the migration of priority pollutants. Soil-moisture samples were also analyzed for priority pollutants.

The analyses were performed by extracting the pollutants from the samples into three fractions - volatiles, base-neutrals and phenolics. After extraction the samples were run on the GC/MS. The data collected was processed by the IQ method for identification and quantification.

Degradation of Oil Fractions

The degradation of oil and the individual fractions were studied using the same two plots as in the priority pollutants study. The extracted oil from each sample was used to perform the fractionation into asphaltenes, saturates, aromatics and polar compounds.

The extraction procedures for oil content available in the literature were not suitable for an oily soil matrix. Hence, an oil content analysis method was developed. Likewise, appropriate sampling and sample preparation methods were developed. The method of analysis used in the fractionation of oil was ASTM D2007.

CHAPTER 5

PROCEDURES

SAMPLING METHODS

Soil Sampling

Sampling is very critical in data collection and analysis. A representative sample must be obtained in order to achieve consistent and meaningful results. Studies were performed to establish a sampling method. The initial sampling method consisted of single samples from each plot using a 1-inch Shelby tube. Analysis of the data showed that high recoveries and consistent results were not obtained. The second method consisted of obtaining five samples from each plot; each sample consisted of a composite of twenty Shelby tube cores. The Shelby tube was 1-inch in diameter, 1-foot long. Variation in the results obtained by this method was attributed to the diameter of the Shelby tube, which was less than the maximum dimension of a significant portion of the agglomerated particles.

In order to reduce the variability, two other methods of sampling were studied. One consisted of using a 3 1/2-inch diameter sampling tube and obtaining three

samples per composite sample and taking three samples per plot. The second method consisted of using a 1 7/8-inch soil sampler, obtaining three composite samples per plot. On analyzing the data obtained from the above two sampling methods statistically, it was found that the method using the 1 7/8-inch sampler gave less variation in the analyses than the 3 1/2-inch diameter sampler. Hence, the method using the 1 7/8-inch sampler was selected. Table 4 shows the variations in the sampling methods.

Monitoring Well Sampling

Samples from the four monitoring wells were obtained using a 2-inch diameter Kemmerer sampler. The sampler consisted of a 3-ft. long stainless steel cylinder with Teflon caps on both ends suspended by a 200-ft. nylon cord. Samples were collected in 500 ml glass bottles prewashed with soap solution and organic free water as outlined by EPA procedures (27).

Vacuum Soil Moisture Samplers (Lysimeters)

The principle involved in the operation of a lysimeter is that a vacuum is applied to the suction side of the tubing as shown in Figure 11. The vacuum is displaced by moisture entering in through the porous cup at the bottom of the lysimeter tube. Initially the water saturates the pores of the ceramic cup, and then water flows into the cup due to the vacuum applied. The sample

Table 4 Statisical Analysis for Choice of Sampler

Sample	% Oil	Mean	Deviation	SS	°F
Medium Sampler (1 7/8" dia.)					
6-1-1	8.4834		0.00187		
6-1-2	8.4250	8.4815	-0.05653	0.006188	2
6-1-3	8.5362	(0.2320)	0.05467		
SS = 0.245244		MSS = 0.122622			
6-2-1	8.3975		-0.02283		
6-2-2	8.2848	8.4203	-0.13553	0.043971	2
6-2-3	8.5787	(0.1708)	0.15337		
6-3-1	7.9491		0.10243		
6-3-2	7.8668	7.8467	0.02013	0.025921	2
6-3-3	7.7241	(-0.4028)	-0.12257		
		8.2495		ESS 0.076030	6
0.012680 EMS analysis					
Large Sampler (3" dia.)					
6-1-1	6.9641		-0.05777		
6-1-2	6.3943	7.0219	-0.62757	0.866857	2
6-1-3	7.7072		0.68533		
SS = 0.103262		MSS = 0.103262			
6-2-1	8.9178		0.40103		
6-2-2	8.0809	8.5168	-0.43587	0.352021	2
6-2-3	8.5516	(0.2272)	0.03453		
6-3-1	8.1635		0.10120		
6-3-2	8.3353	8.0623	0.27300	0.224796	2
6-3-3	7.6881	(-0.2273)			
		7.8670		ESS 1.443676	6
0.240613 EMS analysis					

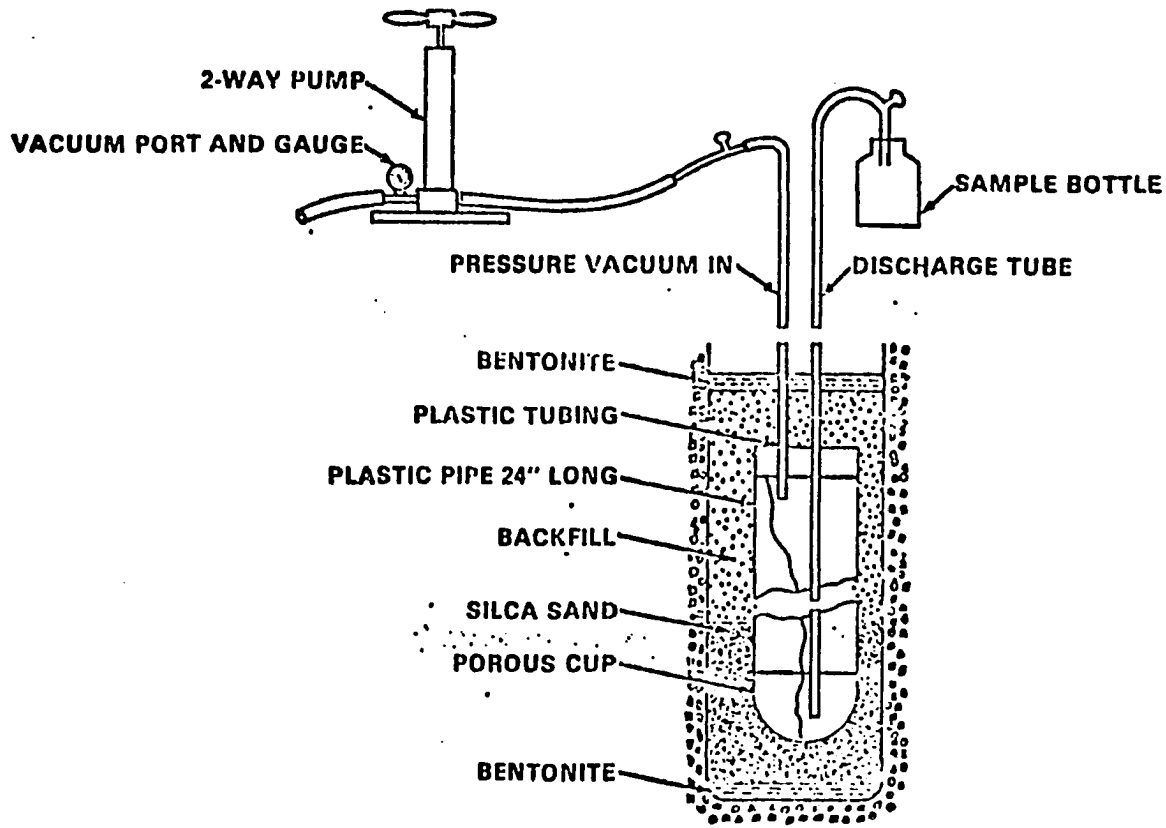


Figure 11. Vacuum soil moisture sampler.

is collected from the ceramic cup by applying a positive pressure thereby displacing the water.

Sludge Sampling

Sludge samples were obtained from the storage tanks by lowering a sampling bottle into the tank and retrieving a sample. Prior to sampling, the mixer was turned on in the well-baffled tank for approximately 12 hours to ensure complete mixing of the tank contents.

ANALYTICAL ANALYSIS

Oil Content Analyses

Oil content is the major control parameter in the land treatment of oil refinery wastes. Hence, an accurate estimation of the oil content is necessary.

There are three steps involved in performing the oil content analysis. They are 1) sampling; 2) sample preparation; and 3) analysis.

Sampling of Soils and Sludges

The sampling method has already been described earlier in this report.

Sample Preparation

Sample preparation techniques are dependent on the sample matrix and the consistency of the sample moisture content. This study involved extensive research with sample preparation techniques for different types of soil

samples. Samples can be classified into four different classes:

1. Samples with moisture content less than the plastic limit, or approximately 18%.
2. Wet samples with moisture content greater than 18%.
3. Sludge samples.
4. Liquid samples.

Samples obtained from the field with a low moisture content were first mixed and quartered several times to obtain approximately 500 gms of soil. Samples were then transferred into a Vitamix 3600, Model 479029, manufactured by Vitamix Corporation, Cleveland, Ohio. This Vitamix has an instant self reversal blade and is made of stainless steel. The sample was blended until it attained a grain size which could pass through a No. 10 sieve, it was quartered until a required sample size was obtained for analysis.

Samples with a moisture content close to or above the plastic limit were difficult to work with because of moisture content. Samples were mixed in a Hobart Mortar mixer, Model C-100 with intermittent scraping of the soil from the sides and the blades to obtain a uniform sample.

The sample was chopped until the particle sizes were small compared to the overall sample size. A flat 1-in. blade stainless steel spatula was used to chop the sample. The sample was quartered several times until the

required sample size was obtained. A drying agent ($Mg(SO_4)$) was mixed with the sample and then pulverized in a mortar and pestle. Liquid samples were thoroughly mixed, and an aliquot of the sample was taken for analysis.

Oil Analysis

There are three basic methods for oil content analyses as mentioned in the "Standard Methods for the Examination of Water and Wastewater", 15th edition and the "Methods for Physical and Chemical Analysis", by EPA. The three methods are 1) gravimetric extraction; 2) infrared spectrometry; and 3) Soxhlet extraction.

The method used in this study is the Soxhlet extraction method, which is the standard method (26) for a continuous extraction process.

Two factors which influence the Soxhlet extraction process are the solvent used and the method of evaporation of the solvent. The different solvents which can be used for the extraction process are:

(1) 15% diethylether and 85% freon

(2) 15% diethylether and 85% methylene chloride

(3) freon

(4) methylene chloride

In the present study, methylene chloride was used due to its extraction capability. The results are shown later

in this section. The method of evaporation was varied from that followed by Standard Methods (26) wherein the solvent was evaporated at 70°C, which resulted in the loss of volatile compounds from the sample matrix. Also, loss of volatiles resulted from the sudden jump in temperature after the methylene chloride or freon evaporated. In order to avoid the above phenomenon, the samples were evaporated on a steam bath until a volume of approximately 15 ml of the solvent was left in the evaporating flask and then transferred to a preweighed aluminum weighing dish. This sample was evaporated at a room temperature in a hood, overnight. An inert gas (N_2) was passed over the sample to drive out any remaining solvent before weighing.

In this study, methods of extraction were studied using freon and methylene chloride. The methods evaluated were:

(1) Freon method as outlined in the Standard Methods Manual
(2) The new method (Appendix A) developed using methylene chloride
(3) The new method (Appendix A) using freon.

The results of this study are given in Table 5. The difference between the methods of evaporation can be observed. Differences in recovery using different solvents for extraction of oil are also exhibited. Freon and

methylene chloride were used as solvents with the new method. The freon method yielded 94% recovery and the methylene chloride method yielded 99% recovery. Therefore, the new method using methylene chloride was chosen.

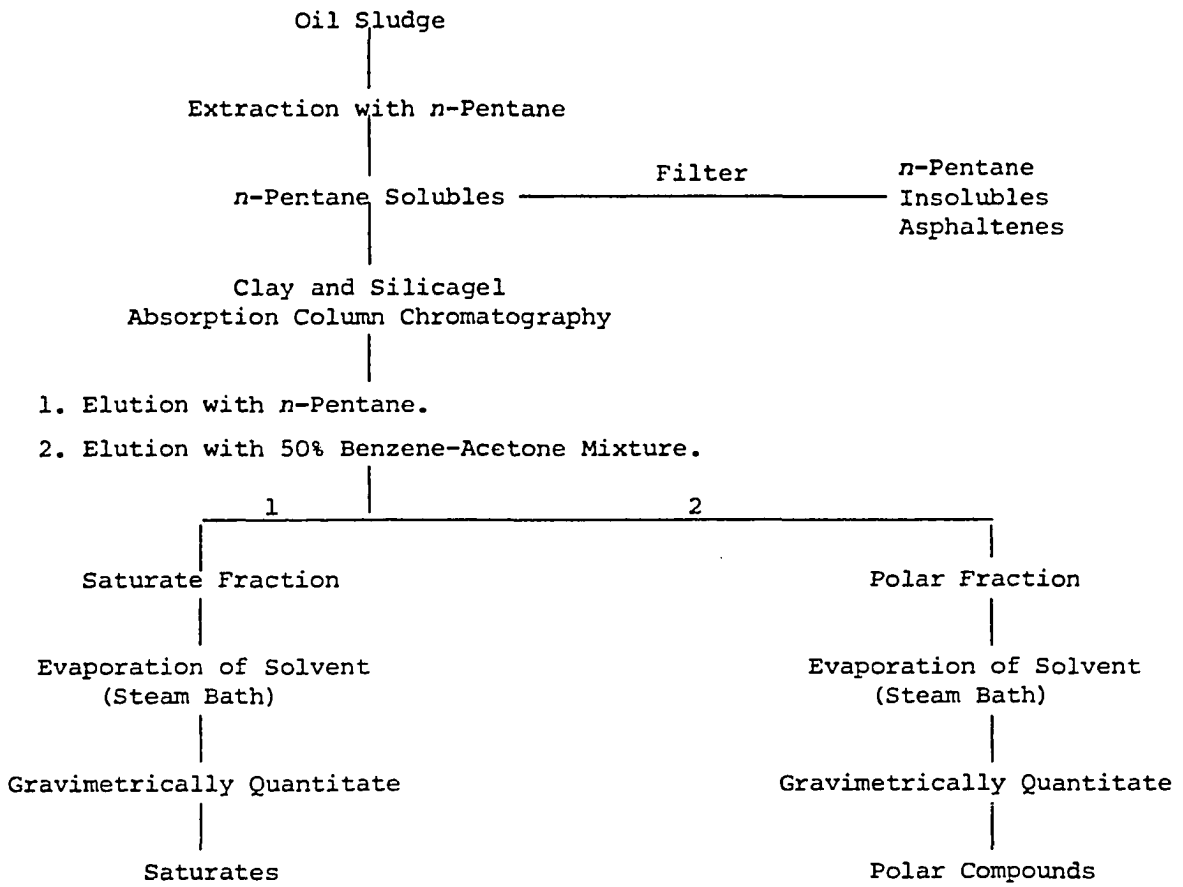
Table 5 Comparison of Oil Content Analysis Methods

#	Solvent and Method of Analysis	% of Oil Recovered on Dry Wt. Basis	Std. Deviation
1	Freon, Std. Method	86%	0.165
2	Methylene Chloride, New Method	99%	0.22
3	Freon, New Method	94%	0.136

Fractionation Analysis

The present study involves the separation of petroleum residues into four fractions, namely, asphaltenes, saturates, aromatics and polar compounds or resins. A flow chart for the extraction is shown in Figure 12. Materials for the analyses were obtained from Forcoven Products Inc., Texas. A diagram of the column and the amount of Attapulgus clay and silica gel used is shown in Figure 13.

Asphaltenes are defined as pentane insolubles that can be separated from a solution of oil in n-pentane and may include insoluble resinous bitumens produced by the oxidation of oil. Polar compounds are material retained on adsorbent clay after percolation of the sample in a



% Aromatics = 100 - % Asphaltenes - % Polar Compounds - % Saturates.

Figure 12. Flow diagram for fractionation analysis.

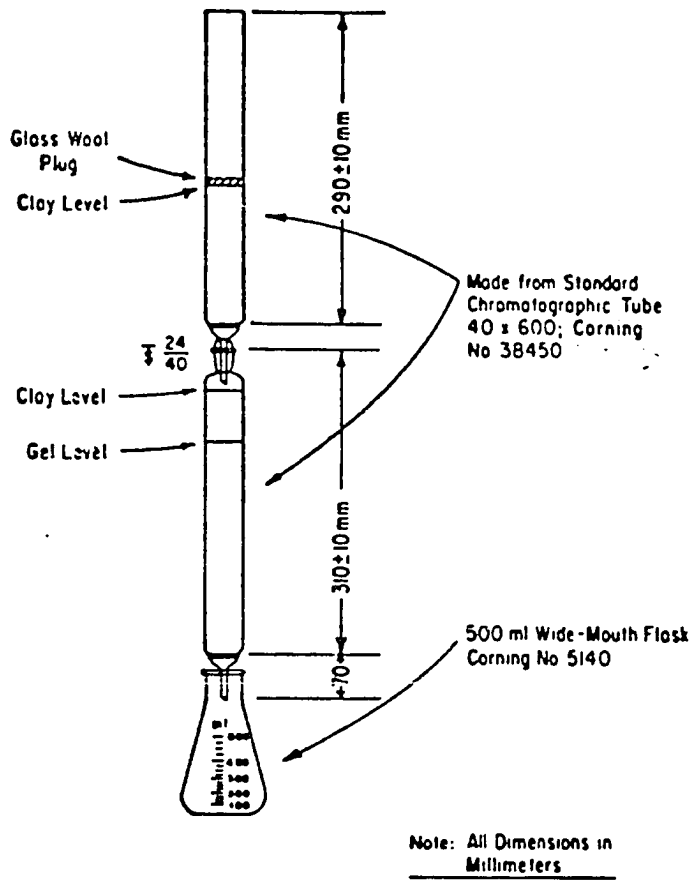


Figure 13. Clay-gel percolating column.

pentane eluent. Aromatics are material that on percolation passes through a column of adsorbent clay in a pentane but adsorb on silica gel. Saturates are material that on percolation in a n-pentane eluent is not adsorbed on either the clay or silica gel. The method used for the separation is the ASTM D2007.

Priority Pollutant Analyses

Priority pollutant analyses were performed using a GC/MS/DS system. Mass spectrometry is one of the most powerful tools in structural elucidation of chemicals. Advent of the combined system of the gas chromatograph and the mass spectrometer provided even more versatility. The GC/MS/DS used in this study consists of a Hewlett-Packard 5985B system with a HP 5740 gas chromatograph, a quadropole mass spectrometer, 21 MX-E series computer with a 7906 dual disk drive and a 2648A CRT terminal and Houston Instrument printer.

The mass spectrometer consists of dual stage diffusion pumps and foreline pumps which together maintain the vacuum to about 10^{-7} torr. The ion source consists of an electrically heated tungsten filament which emits electrons for bombardment on the sample molecules causing ionization of the sample molecules. The quadropole mass analyzer separates the ions on the basis of their m/e values by means of electric fields. On reaching the

electron multiplier these ions generate secondary ions and the secondary ions are collected on the cathode and the ion currents are recorded. An ion current 10^{-19} amps corresponds to an arrival rate of 1 ion per second. The ion current or peak intensities are then plotted as a Spectrum Manipulation of the data and can be done at this stage in terms of quantification and library searching and peak matching.

The sample preparation (27) for GC/MS analysis consisted of extracting approximately 10 gms of a sample in a Soxhlet extraction apparatus with CH_2Cl_2 (methylene chloride). The sample after extraction was concentrated down to a volume of approximately 2 mls. This fraction constituted the neutral extract. A part of this extract (0.5 mls) was placed in a separatory funnel, water was added, and the pH was raised to 13 - 14 with NaOH. The sample was extracted with three 60 ml portions of CH_2Cl_2 and the extract concentrated to a volume of approximately 2 mls. This constituted the base-neutral extract. The fraction remaining in the separator funnel was acidified to a pH 2 to 3 with HCL and extracted with three 60 ml portions of CH_2Cl_2. This extract was concentrated to a volume of approximately 2 mls, which constituted the phenolics extract. All three extracts were passed through columns of anhydrous Na_2SO_4 for drying. The three samples were then run on a GC/MS/DS for volatiles,

base-neutrals and phenolic compounds.

The column and conditions used on the GC for each of these analyses are given in Table 6. The list of priority pollutants studied are in Table 7.

Standards were run at the beginning of each set of analyses. Similarly, the mass-spectrometer was tuned with PFTBA (perfluorotributylamine) at the beginning of each day. The standards were then identified from the mass spectrum of each peak obtained in the chromatogram. The unknown samples were then run and stored on the data disk. Once all the samples were run, a standard file library of all the compounds was created using the computer IQ program written for identification and quantification. Separate files were created for volatiles, base-neutrals and phenolics. The sample data file was then set up for matching and quantification. The print out was analyzed, and the concentrations were calculated based on the response factors of the standards.

Comparison of Identification and Quantification Techniques in GC/MS/DS

The reason for developing an Identification and Quantification technique was that the existing 5985B GC/MS/DS system did not have the capability of performing the task. The PBMQ and HIBE methods did not follow EPA protocols. The speed at which the analysis was performed by the IQ method was better than the PBMQ and HIBE

Table 6 Column Conditions for GC/MS Analysis

Conditions	Volatiles	Base-Neutrals	Phenolics
Initial Temp.	60°C	50°C	60°C
Initial Hold Time	3 min.	1 min.	1 min.
Ramp Rate 1	8°/min.(1)*	30/min.(2)*	30/min.(2)*
Ramp Rate 2	-	8°/min.	8°/min.
Final Temp.	160°C	300°C	270°C
Detector Temp.	200°C	200°C	200°C
Injection Temp.	175°C	250°C	200°C
Time of Run	25 min.	40 min.	20 min.
Hold Time	3 min.	2 min.	2 min.
Gas Flow	24 mls/min.	14 mls/min.	14 mls/min.
Column	Carbopack C (60-80 mesh) Coated with 0.2% Carbowax 1500	SE-54, DB-5 1.0μ,0.32μ, 30 meters	SE-54, DB-5 1.0μ, 0.32μ, 30 meters
Detector	MS	MS	MS

Note * ( ) time in minutes

Table 7 List of Priority Pollutants

Purgeables	Phenolics
1,2-Trans-Dichloroethylene	2-Chlorophenol
Chloroform	Phenol
1,1,1-Trichloroethane	2,4-Dichlorophenol
1,2-Dichloroethane	2-Nitrophenol
1,1-Dichloroethane	p-Chloro-m-cresol
Carbon Tetrachloride	2,4,6-Trichlorophenol
Dichlorobromomethane	2,4-Dimethycphenol
1,2-Dichloropropane	2,4-Dinitrophenol
Benzene	4,6-Dinitro-o-cresol
Trichloroethylene	4-Nitrophenol
Chlorodibromomethane	Pentachlorophenol
1,1,2-Trichloroethane	
Methylbromide	
Bromoform	
1,1,2,2-Tetrachloroethane	
Tetrachloroethylene	
Toluene	
Chlorobenzene	
Ethylbenzene	

(continued)

Table 7 List of Priority Pollutants (continued)

Base Neutrals	
1,3-Dichlorobenzene	N-Nitrosodiphenylamine
1,4-Dichlorobenzene	Hexachlorobenzene
Hexachloroethane	4-Bromophenyl phenylether
1,2-Dichlorobenzene	Phenanthrene
Bis(2-chloroisopropyl)ether	Anthracene
Hexachlorobutadiene	Dimethylphthalate
1,2,4-Trichlorobenzene	Diethylphthalate
Naphthalene	Fluoranthene
Bis(2chloroethyl)ether	Pyrene
Hexachlorocyclopentadiene	Di-n-butylphthalate
Nitrobenzene	Benzidine
Bis(2-chloroethoxy)methane	Butylbenzylphthalate
2-Chloronaphthalene	Chrysene
Acenaphthalene	Bis(2ethylhexyl)phthalate
Acenaphthene	Benzo(a)anthracene
Isophorone	Benzo(b)fluoranthene
Fluorene	Benzo(k)fluoranthene
2,6-Dinitrotoluene	Benzo(a)pyrene
1,2-Diphenylhydrazine	Indeno(1,2,3-cd)pyrene
2,4-Dinitrotoluene	Dibenzo(a,h)anthracene
	Benzo(g,h,i)perylene

methods. For a minicomputer like the 21 MX-E, the analysis time was considerably faster than with the PBMQ and HIBE methods.

The present study consisted of a comparison of the library spectra of known compounds with that of unknown standard compounds. This also included the quantification of the identified compound. Three different identification and quantification methods were studied, namely the EPA method, McLafferty's PBM method and the Hites-Biemann method. Computer programs for all three methods were written during this study so that the analysis could be performed on the locally available GC/MS/DS. The EPA method of identification and quantification of known compounds in unknown samples consists of three conditions. First, the characteristic ions for a compound must be found to maximize in the same spectrum (e.g. D10 anthracene - the characteristic ions are 188, 94, and 80). Second, the time at which the peak occurs in the GC run must be within ±1 minute for the standard run. Finally, the ratios of the three peak intensities must agree with that of the standard compound within ±20%. A computer program was written which approximates the above conditions and identifications were done using standard compounds and unknown samples.

To compare the three methods, a mixture of seven standard compounds were used in addition to the internal

standard. The three programs were designated as IQ (EPA method), PBMQ (McLafferty's PBM method) and HIBE (Hites-Biemann method). The concentration (amount injected in ng) of the compounds chosen for this study ranged from 5-6 ng to 400 ng. The compounds were selected so that they represented a wide range of retention times in a base-neutrals run of 40 minutes. The process by which the search was set up is as follows:

Standards Injection into GC

GC/MS Spectra Recorded

Creation of Standards Library

Injection of Sample into GC

Sample GC/MS Recorded

Comparison of File Sample Now Created

Searching and Matching with Library

Printing of Mass Spectra of Known, Unknown and Difference Spectra

Data Manipulation

QUALITY CONTROL

A quality control/assurance program was developed for this study. The QA/QC program covered the following aspects of the study.

(1) Sampling

(2) Oil Content Analysis

(3) Fractionation Analysis

(4) GC/MS Analysis

Sampling

The method of sampling in the field affects the results of the study. A representative sample was procured by taking 10 core/sample and 3 samples per plot. Results of the sampling method are given in Table 4. If the replicate samples analyzed for oil content did not yield consistent values within a ±5% error, then the samples were rerun to check the analysis procedure. If the analysis was still not consistent, then the plots were resampled for analysis immediately.

Oil Content Analysis

Background soil samples were obtained from the field to represent the soil matrix to which the oily residues were applied. The background soil samples were spiked with a known amount of oily residue. The samples were extracted using the revised Soxhlet extraction procedure. The results are tabulated in Table 8. The mean recovery was found to be 96.2%.

Table 8 Oil Recovery from Spiked Samples

No.	% Oil Recovered	% Oil Applied
1	9.37	10
2	9.78	10
3	9.69	10
Mean	9.62	

Fractionation Analysis

Reference standards for quality control were obtained from EPA through their quality assurance program. The reference standard used was the Kuwait Crude Oil. Two analysts performed the extractions. Results of the recoveries by the two analysts are presented in Tables 9 and 10. The method of analysis was ASTM - D2007. The results show that the variation between analysts was not significant.

Gas Chromatography/Mass Spectrometry Analysis

The GC/MS system was tuned on a daily basis. The compound used for calibration of the instrument was perfluorotributylamine (PFTBA). DFTPP (decafluorotriphenylphosphine) standards were also run to check the relative ion abundances. Blank samples were run for every set of priority pollutant analyses. The column used in the GC were baked overnight so that the contaminants were driven out. Similarly, the mass spectrometer source was also elevated to a temperature of 274°C to get rid of any contaminants. A blank chromatogram was run.

Table 9 Results of Analysis of Kuwait Crude Oil for Quality Control - Analyst 1

No.	Saturates	Aromatics	Polar Compounds	Asphaltenes
1	39.10	40.0	16.80	4.1
2	30.20	52.0	13.40	4.4
3	35.10	47.4	14.50	4.0
4	36.10	46.0	13.90	4.0
5	35.60	45.5	14.60	4.3
6	36.30	44.8	14.50	4.4
7	35.80	45.6	14.30	4.3
Mean	35.46	45.9	14.57	4.21
EPA Ref. Value	32.30	47.6	16.90	3.20

Table 10 Results of Analysis of Kuwait Crude Oil for Quality Control - Analyst 2

No.	Saturates	Aromatics	Polar Compounds	Asphaltenes
1	33.00	48.4	14.30	4.3
2	32.80	47.7	15.30	4.2
3	36.00	44.9	14.90	4.2
4	35.60	44.8	15.20	4.4
5	32.30	47.7	15.70	4.3
6	33.60	47.0	15.20	4.2
7	34.20	46.4	15.20	4.2
8	33.80	47.0	14.90	4.3
9	33.50	46.7	15.70	4.1
10	32.00	48.4	15.10	4.5
Mean	33.68	46.9	15.15	4.27
EPA Ref. Value	32.20	47.6	16.90	3.2

CHAPTER 6

RESULTS AND DISCUSSION

OIL CONTENT AND FRACTIONATION

Introduction

The land treatment process performance study was quantified in terms of the following selected variables: oil content and fractions (asphaltenes, saturates, polar compounds and aromatics). In order to evaluate the above variables sampling, sample preparation and analysis methods were developed. The methods developed are presented in the methodology section of the report. Presented in this section are the results of this study and a discussion of the results obtained on oil content and fractionation by the land treatment process. This section is divided into two divisions, the first of which deals with the results and discussion of the oil content data and the second with the fractionation data.

The analysis of the above variables (oil content and fractions) provides a quantitative evaluation of the performance of the land treatment process at this specific site and for the specific waste. The findings presented herein can be extrapolated in whole or in part

depending on relative changes in the site, climate and weather conditions.

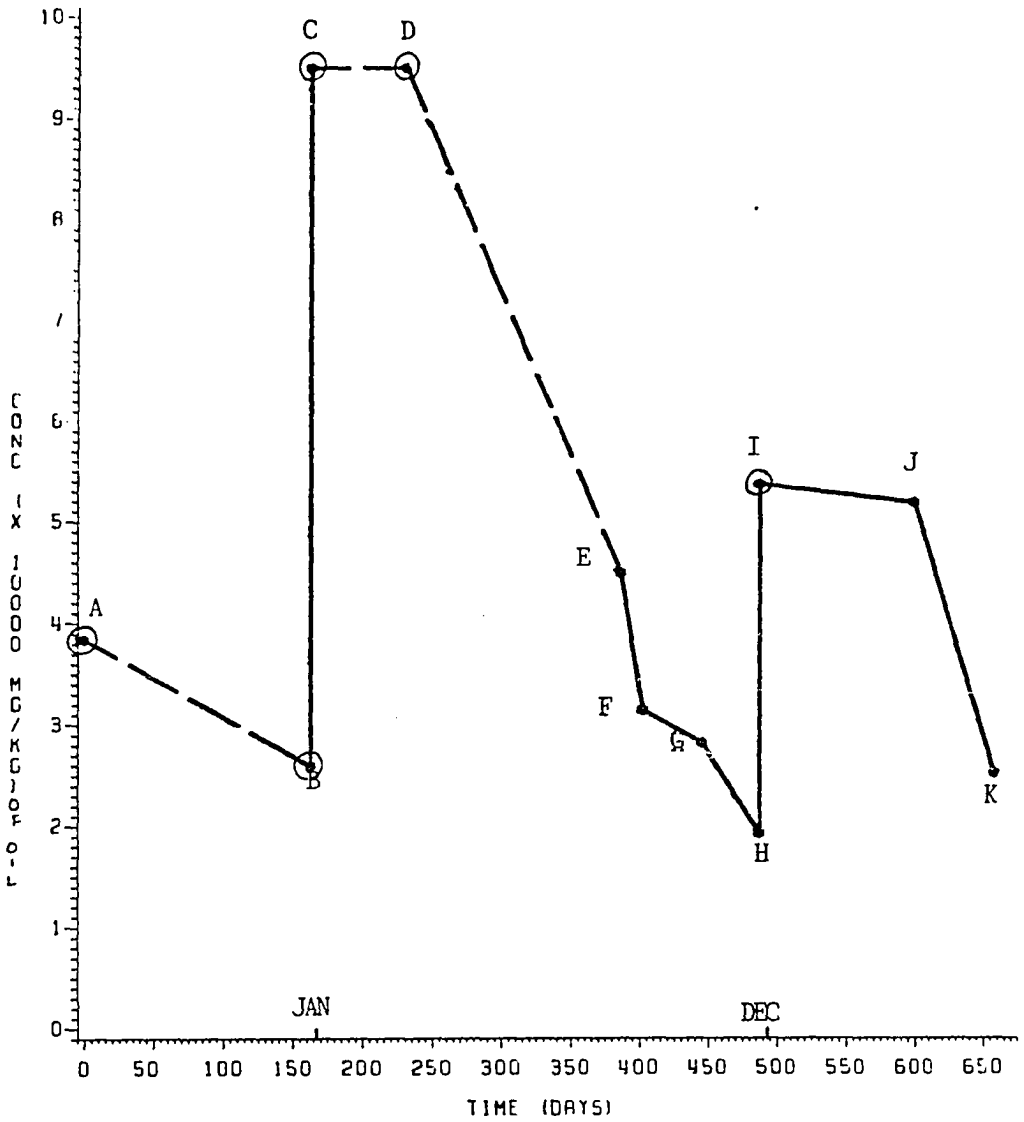
Results and Discussion of the Oil Content Data

This section deals with the analysis and discussion of the oil content data collected. The degradation of oily sludges was followed over a period of time, and the oil losses were computed. The rate of degradation of the oily sludges was also studied. The problems encountered during this study are also discussed.

The results of the oil content data are presented in Figures 14 and 15. Application dates and percent oil applied for plots 30 and 35 are presented in Table 11. Raw data for the oil content and fractionation are presented in Appendix B.

Table 11 Application Rates of Oily Residues

Plot #	Application Date	% Applied
30	8/19/81	3.85
30	1/19/82	6.90
30	12/20/82	3.45
35	8/19/81	6.15
35	1/19/82	6.81
35	12/20/82	5.75



⊙ Calculated points • Experimentally measured points

Figure 14. Degradation of oily residues with time - plot # 30.

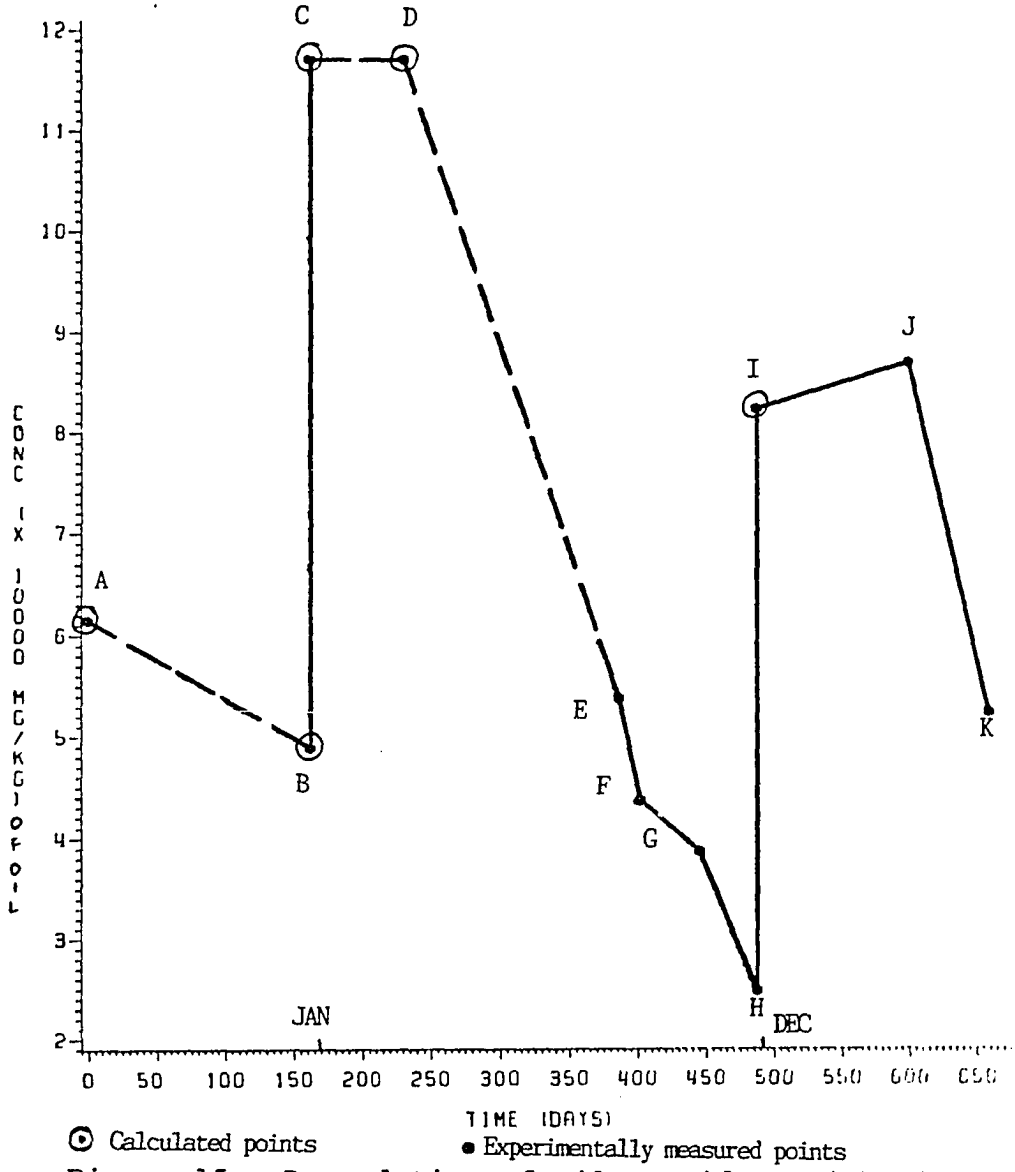


Figure 15. Degradation of oily residues with time - plot # 35.

Analysis of the data was performed by dividing the entire study into two time periods, Phases 1 and 2. The first time period consisted of 488 days and the second 171 days. The reason for two different lengths of time in Phases 1 and 2 was due to weather conditions which prevented adherence to the nominal loading frequency of once per year. In the initial phase two applications were made. The reason for two applications in Phase 1 was that plots could not be loaded with oily residues at the desired loading rates without exceeding the field capacity of the soil. Following the initial application heavy rains prevented tilling of the plots; therefore, the immediate addition of the balance of the oily sludge to fulfill the desired loading rate was not possible. The remaining sludge was applied after a period of five months when the soil was tillable at point B. In Figures 14 and 15, points A to H correspond to Phase 1 and points I to K correspond to Phase 2.

During Phase 1 of the project from points A to E (excluding point E) several problems, in addition to weather conditions, were encountered in sampling, sample preparation and oil content analysis. Oil recoveries were inconsistent during Phase 1. Only a small fraction of the oil applied was recovered as shown in Table 12. Hence, points A to E as represented by dashed lines, were calculated and not experimentally measured points. The

calculations were based on trends observed in the second phase during similar time periods and weather conditions. The inconsistencies in oil recoveries were overcome by the development of new sampling, sample preparation, and oil content analysis methods as explained in the procedures section of this dissertation. From point E on all points were experimentally measured points with the exclusion of the application at point I. Point I was determined by adding the amount of oil applied and the amount of oil remaining from the previous application at point H. The amount of sludge to be applied was determined from the oil content of the sludge, soil density and the loading rate and frequency desired.

Table 12 Oil Recoveries Before Methods Development

Plot #	Amount of Oil Applied (%)	Amount of Oil Recovered (%)
1	2.17	0.287
5	1.67	0.392
10	3.0	0.399
13	0.83	0.091
24	1.5	0.242

Figures 14 and 15 show a period between points I and J in which the total oil content did not change appreciably. During this period the plots could not be tilled due to saturated soil conditions. The above period also coincided with the winter months. The cause of the low

overall degradation rates could be the result of saturated soil conditions, which presumably resulted in anoxic conditions, and/or low temperatures. Since degradation was inhibited during winter the system acted as a storage unit for the sludges applied during cold temperature. As conditions improved, degradation commenced and/or accelerated.

Oil losses were calculated for Phase 1 and Phase 2 for plots 30 and 35. The results of the oil losses are presented in Table 13. Oil losses were the highest from points E to H and J to K during the summer and fall months. The mean oil losses during Phase 1 and 2 were 81.5% and 47.5%, respectively.

Several factors were involved in affecting the difference in oil losses between Phases 1 and 2. Phase 1 consisted of a period of 488 days and Phase 2 of only 171 days. The initial application in Phase 1 was made in August; this allowed time for degradation of the oil prior to low temperature winter conditions; whereas Phase 2 was predominantly during the winter when low temperatures persisted, resulting in a period of minimal degradation. For these reasons the losses were greater than Phase 2.

Overall oil losses were calculated for the entire period of study. The results are presented in Table 14. Losses for plots 30 and 35 were 82% and 72%, respective-

Table 13 % Oil Losses

Plot #	Phase 1	Phase 2
30	82	53
35	81	42
Mean	81.5	47.5

Table 14 Overall Losses of Oil Fractions

(Wt. %)	Plot 30	Plot 35
Oil Applied	14.2	18.71
Sample	2.51	5.24
Loss	11.69	13.47
% Loss	82	72
Asph. Applied	0.31	0.44
Sample	0.11	0.28
Loss	0.20	0.16
% Loss	65	36
Sat. Applied	7.53	9.57
Sample	0.84	2.17
Loss	6.69	7.40
% Loss	89	77
Arom. Applied	4.28	5.76
Sample	0.84	2.17
Loss	6.69	7.40
% Loss	83	81
Pol. Applied	2.07	2.93
Sample	0.87	1.67
Loss	1.20	1.26
% Loss	58	43

ly. The above results were compared with data presented in the literature. Comparison of the results with literature data (Table 15) showed a good agreement of total

Table 15 Oil Losses - Comparison with Reported Values

Reference	% Oil Losses/Year
Huddleston and Myers	72
Raymond et al.	48.5-90
Present study	45-81

oil losses. The oil losses reported in the literature ranged from 48.5% to 81%. The data obtained from the other 43 plots of the land treatment project showed that oil losses increased with an increase in loading rates and a decrease in loading frequencies (28).

Oil content data from the unsaturated zone is shown in Table 16. No significant migration was found to occur. Rate coefficients for oil losses were computed for first and second order reaction kinetics and the adequacy of fit determined for both. Since the results of the entire land treatment study, of which this study was a part, show that as the concentration of the oily sludges in the soil increases the oil losses increase, then the losses follow either first or second order kinetics. Evaluation of the regression plots obtained for first and second order reaction kinetics yielded correlation coefficients (r^2) of 0.95 and 0.96 for plot 30 and

Table 16 Oil Content Analysis of the Unsaturated Zone

Plot No.	Depth of Sampling	Date	Oil Content Wt. % on Dry Wt. Loss
30-1	12-16"	4/7/82	0.1326
30-2	12-16"	4/7/82	0.2930
35-1	12-16"	4/7/82	0.3294
35-2	12-16"	4/7/82	0.6301
30-1	36-42"	9/30/82	0.0379
30-2	60-64"	9/30/82	0.0295
35-1	24-28"	9/30/82	0.0544
35-2	34-40"	9/30/82	0.0204
35-3	46-52"	9/30/82	0.0862
35-4	60-64"	9/30/82	0.0250
30-1	24-30"	7/15/83	0.1960
30-2	38-42"	7/15/83	0.1462
35-1	24-30"	7/15/83	0.1482
35-2	42-48"	7/15/83	0.0500

0.97 and 0.99 for plot 35, respectively. The data for the above results are presented in Table 17. The results indicate that correlation coefficients were comparable for first and second order reaction kinetics. Since most biological reactions which occur are generally first

Table 17 Correlation Coefficients for Rate Equations

Plot #	Time/Days	Conc. %(dwb)	ln of Conc.	1/Conc.
30	0	4.49	1.50	0.223
	16	3.15	1.15	0.318
	59	2.85	1.05	0.351
	101	1.94	0.66	0.516
Correlation Coefficient		31%	95.2%	95.9%
35	0	5.37	1.68	0.186
	16	4.37	1.47	0.229
	59	3.87	1.35	0.791
	101	2.48	0.91	1.10
Correlation Coefficient			96.9%	99.3%

order or pseudo first order, first order kinetics was assumed and those rate constants were computed. The results of the computation are presented in Table 18. The are presented in Table 18. The rate constants for Phases 1 and 2 were found to be similar. The values were found to be 0.0073 day^{-1} and 0.00699 day^{-1} for Phase 1 and 0.0124 day^{-1} and 0.0086 day^{-1} for Phase 2.

Table 18 Rate Coefficients "K" Oily Residue Degradation

Plot #	Phases of Study	
	1* (day^{-1})	2* (day^{-1})
30	0.0073	0.0124
35	0.00699	0.0086
Mean	0.007	0.0105

* Phase 1 = 488 days Phase 2 = 171 days

Results and Discussion of Fractionation

It was deemed desirable to study the degradation of individual fractions from the total oil; therefore, the oil was further fractionated into asphaltenes, saturates, aromatics and polar compounds to study the behavior of the individual fractions. The following section deals with the analysis and discussion of the data obtained for the above fractions. The losses and the rate of degradation of the fractions are evaluated and discussed. The results of fractionation of oily residues are presented in Figures 16 through 23. Table 19 shows the loading

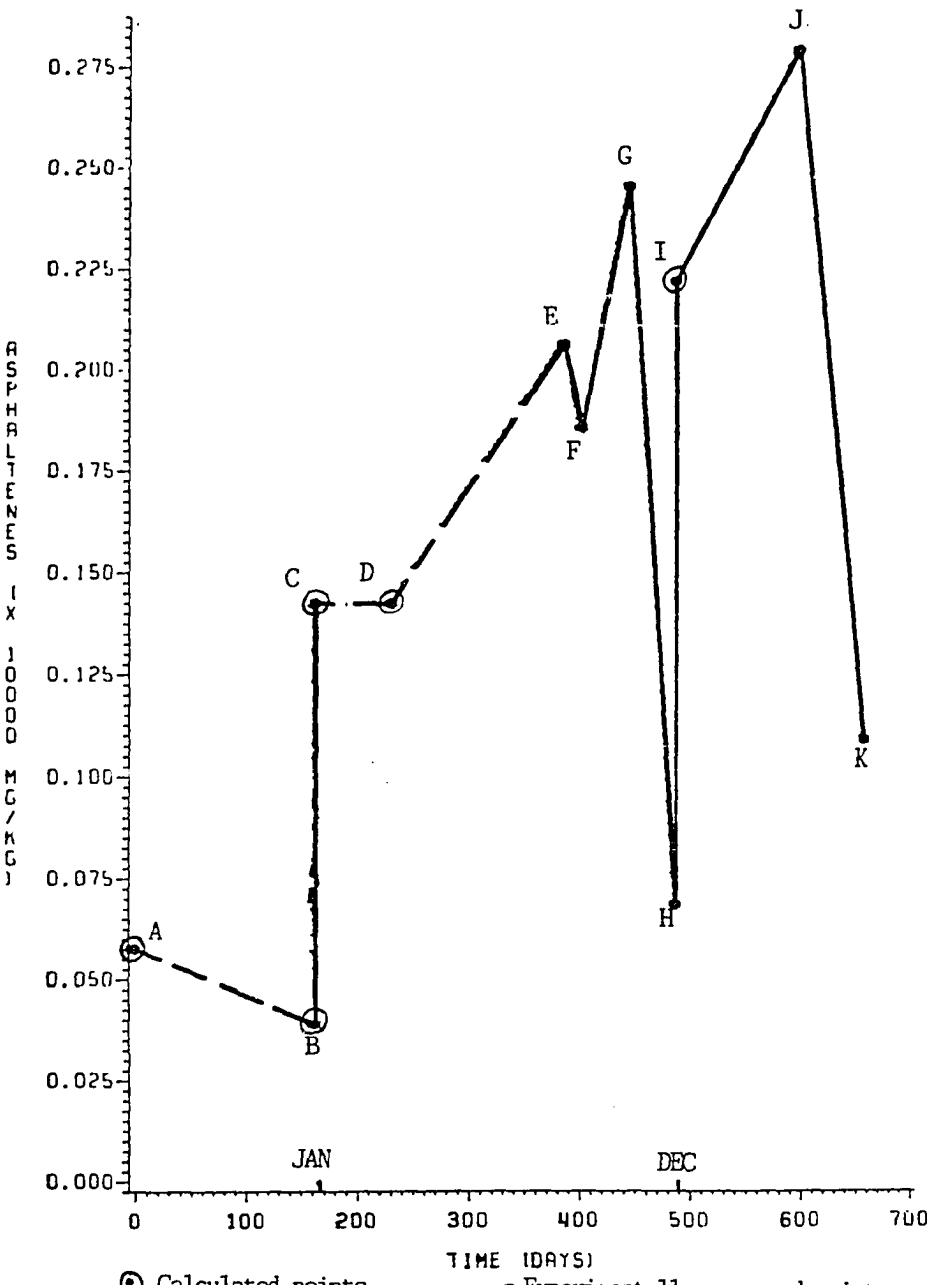


Figure 16. Variation of asphaltenes with time - plot # 30.

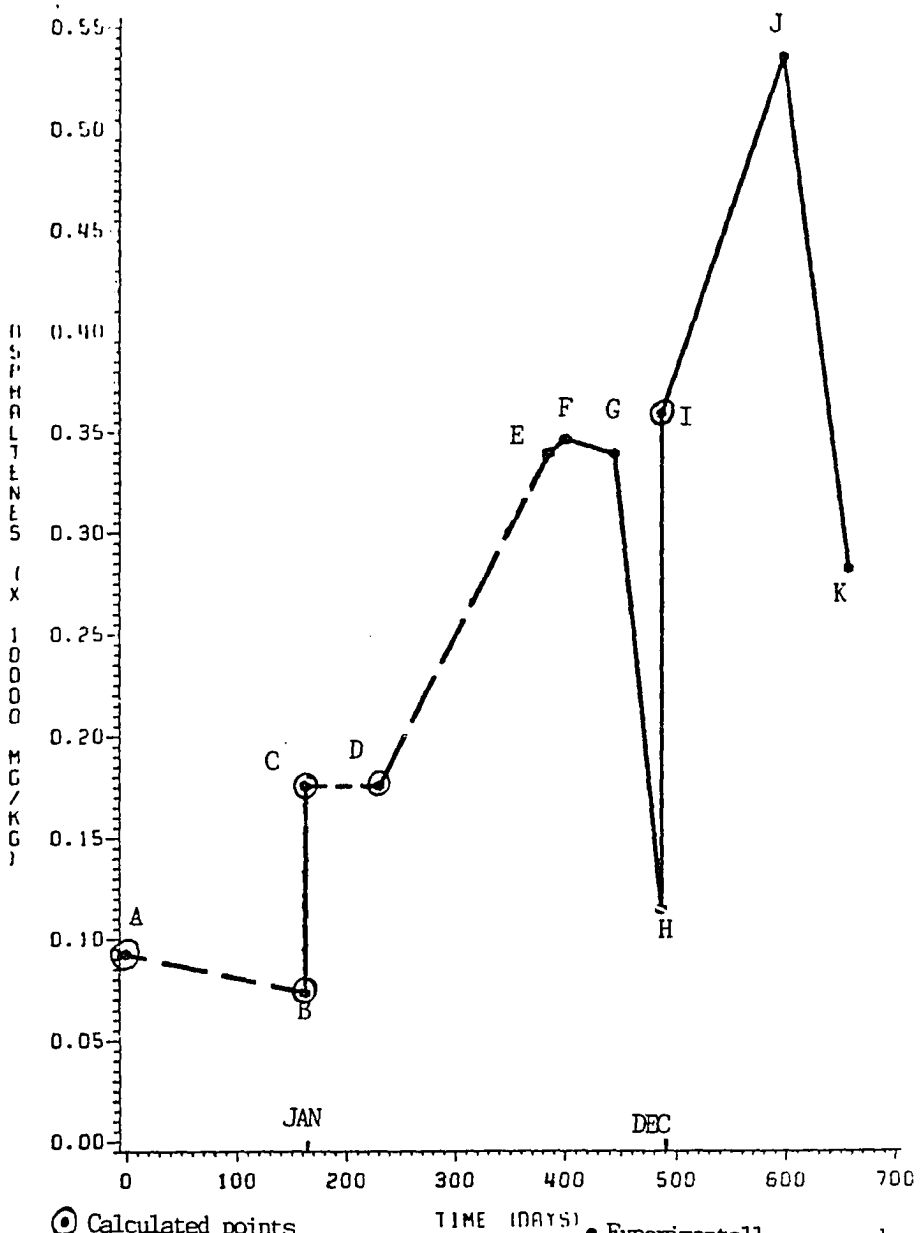


Figure 17. Variation of asphaltenes with time - plot # 35.

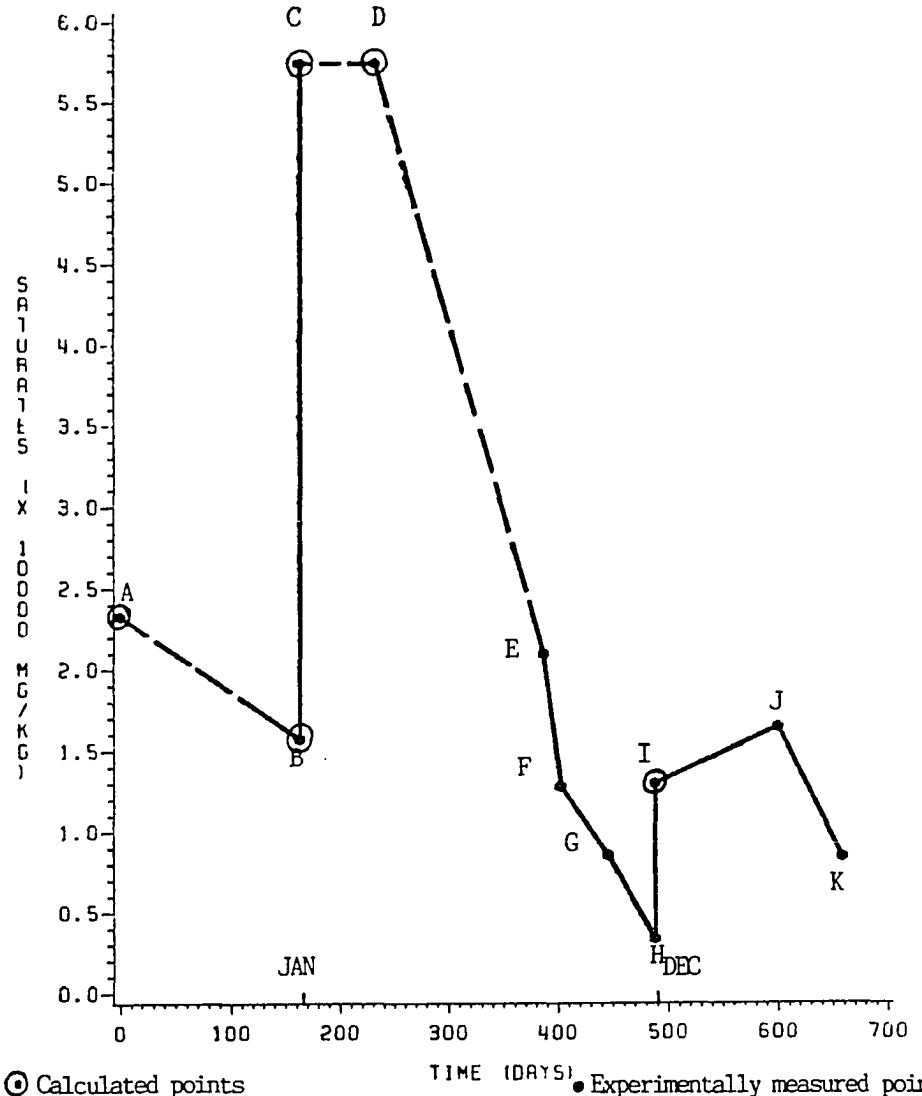


Figure 18. Variation of saturates with time - plot # 30.

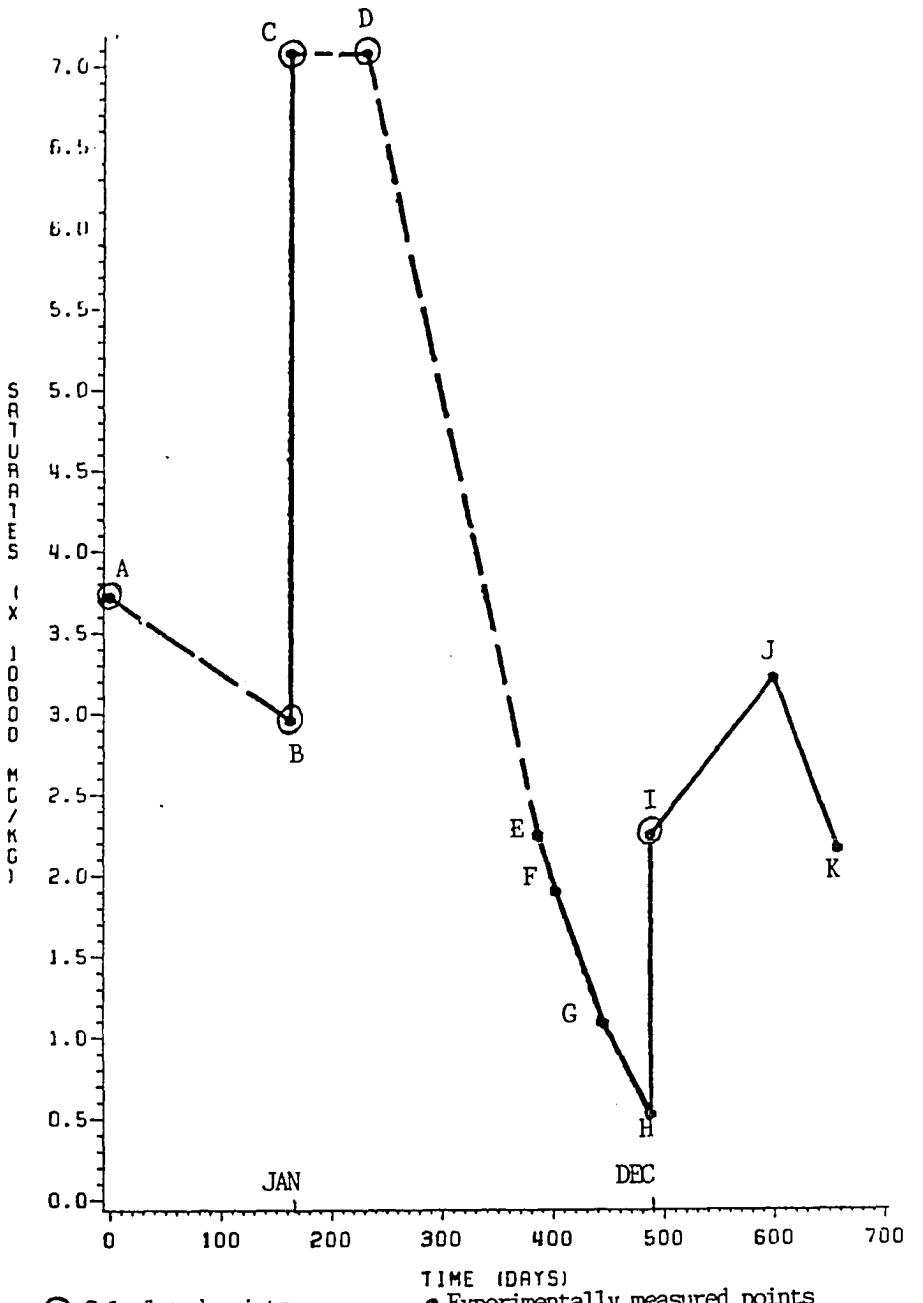


Figure 19. Variation of saturates with time - plot # 35.

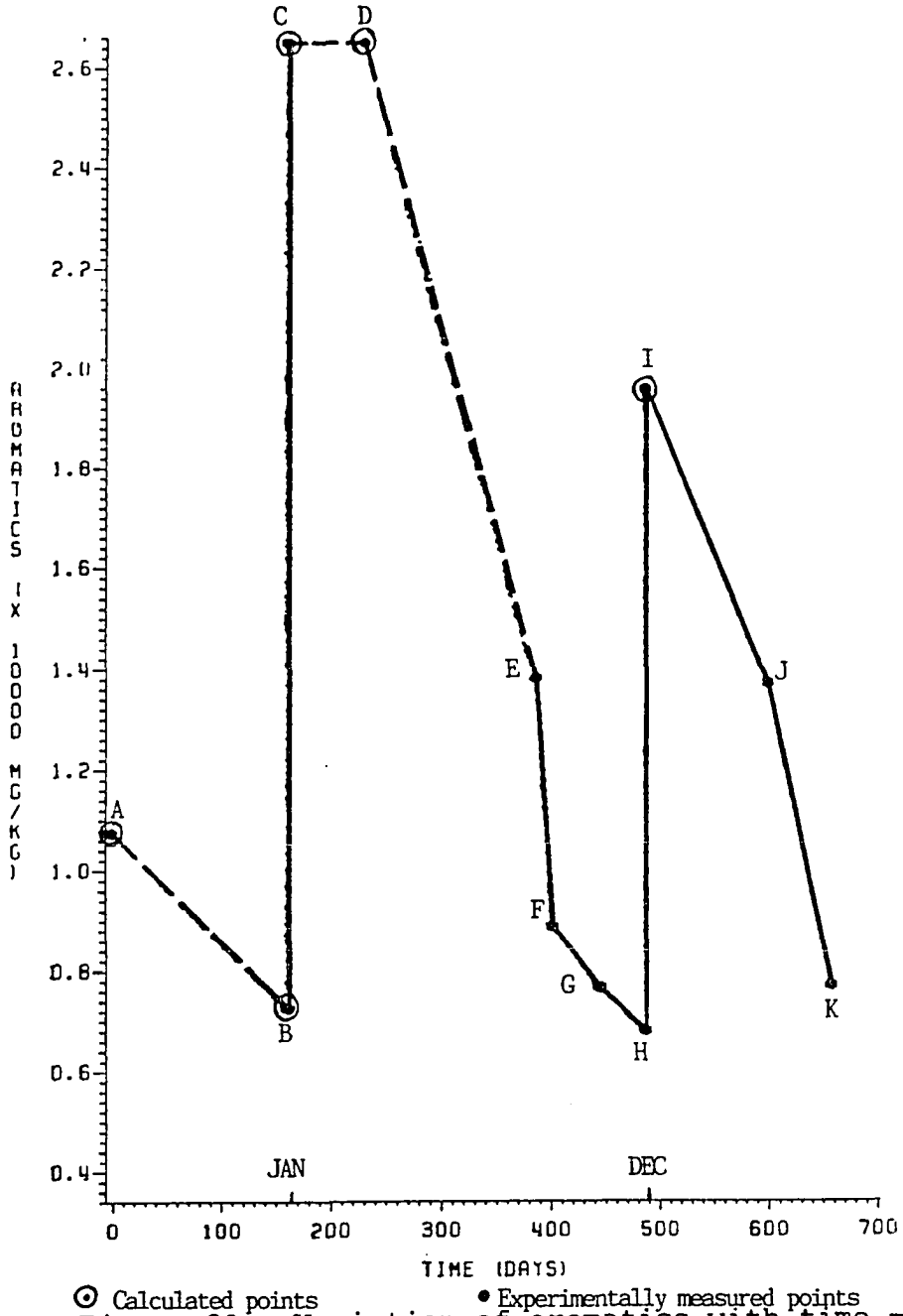


Figure 20. Variation of aromatics with time - plot # 30.

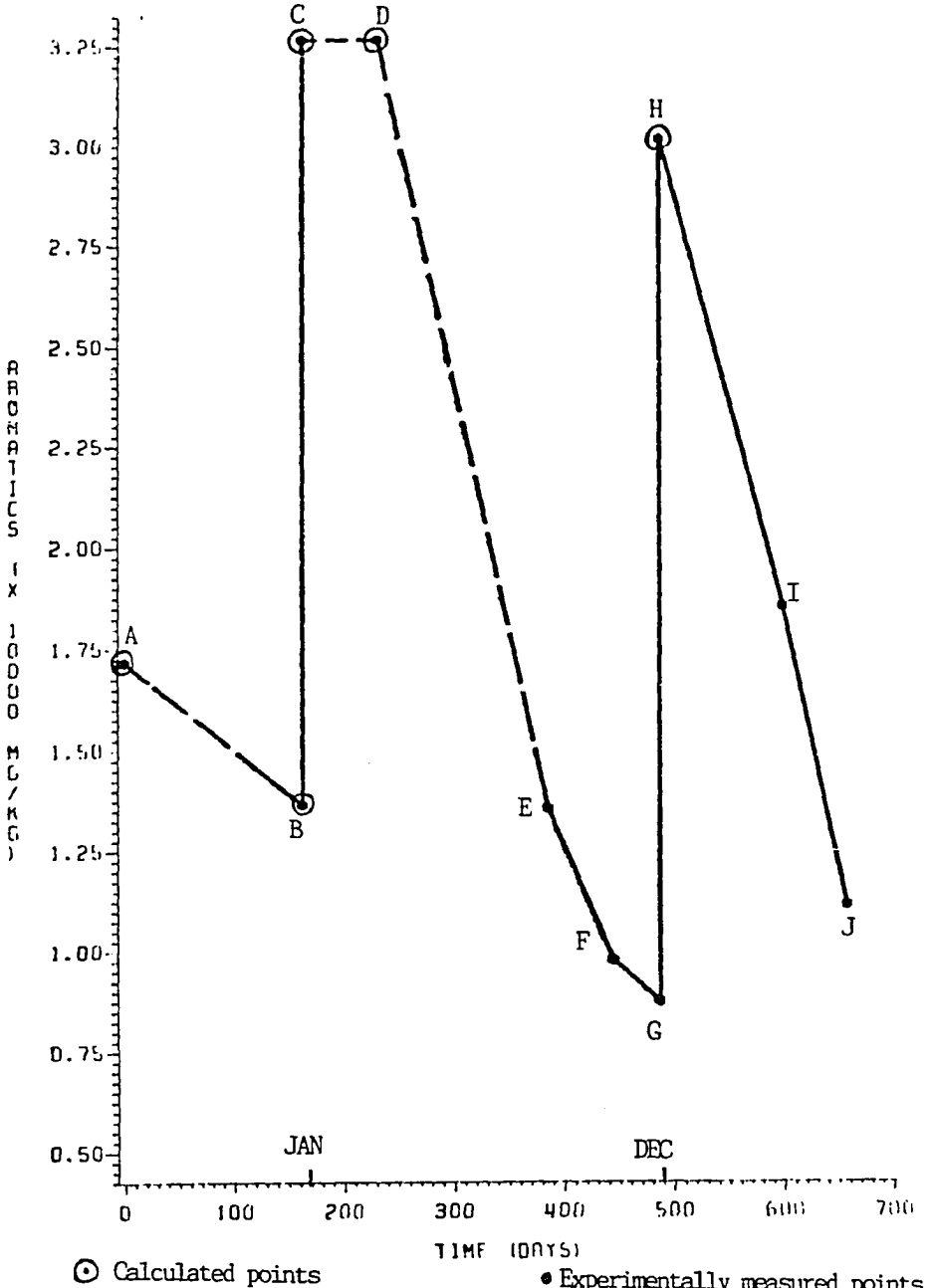


Figure 21. Variation of aromatics with time - plot # 35.

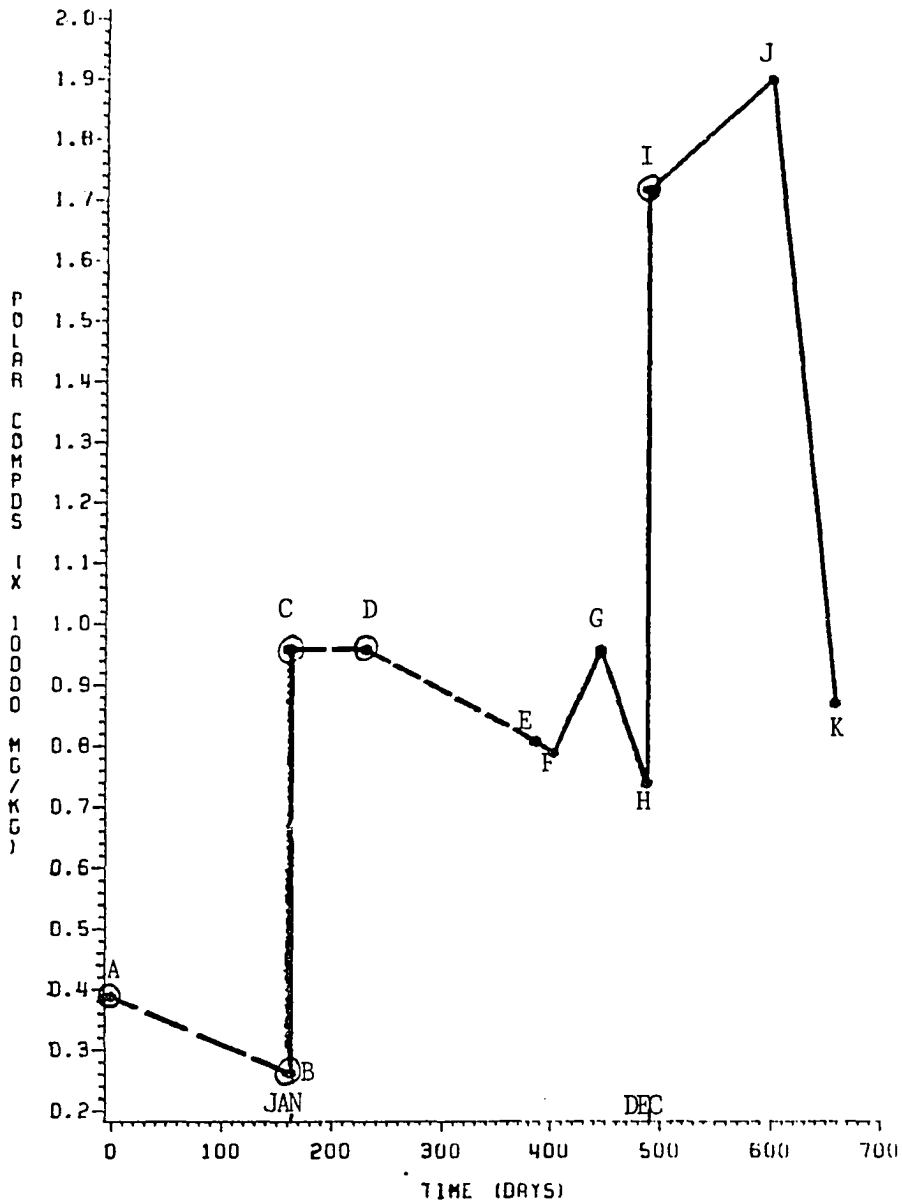


Figure 22. Variation of polar compounds with time - plot # 30.

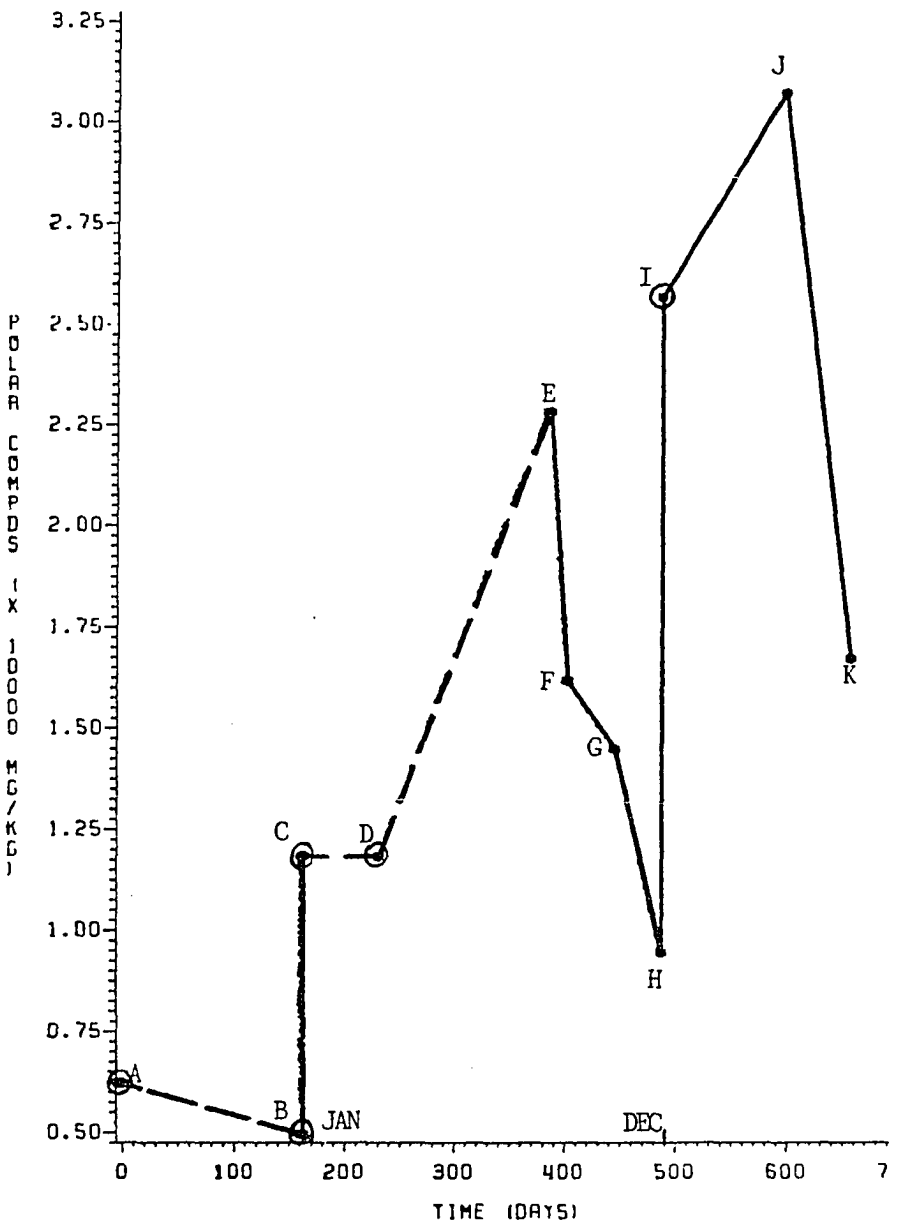


Figure 23. Variation of polar compounds with time - plot # 35.

rates and the application dates of oil fractions. The raw data for the fractionation are presented in Appendix B. Each mean data point shown in Figures 16 through 23 consisted of three data points. Analysis of the fractionation data showed variations. An error of 20% was assumed reasonable. Based on this assumption the data was reviewed and two data points were found to be outside the range of the mean ±20%. Before the two data points

Table 19 Loading Rates of Oily Fractions (%)

Plot #	Application Dates	Asphaltenes	Saturates	Aromatics	Polar Compounds
30	8/19/81	1.5	60.5	27.9	10.1
30	1/19/82	1.5	60.5	27.9	10.1
30	12/20/82	4.43	30.15	17.15	28.26
35	8/19/81	1.5	60.5	27.9	10.1
35	1/19/82	1.5	60.5	27.9	10.1
35	12/20/82	4.43	30.15	17.15	28.26

were eliminated, they were compared with the data for all four fractions to determine if these two points coincided with the trends found in the rest of the data. Since they did not fall within the trend and were outside the range they were considered outliers and eliminated.

Observation of Figures 16 and 17 show that the asphaltenic fraction (pentane insolubles) at point E was greater than the sum of the total amount of asphaltenes applied at points A and B in plots 30 and 35. A similar

trend was observed during the dormancy period i.e. points I to J. Although these increases were not expected, they can be explained. 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.

Walker et al., (1976) characterized the pentane insoluble fraction using computerized mass spectrometry as carboxylic acids, ketones, esters and porphyrins. Waksman (1927) has shown that anaerobic decomposition produces various acids, such as acetic, butyric and lactic, and alcohols, such as ethyl and butyl and in some cases acetone. Okinsky and Umbreit (1959) showed that the anaerobic decomposition of aromatic ring compounds produces acids, saturated hydrocarbons, alcohols and ketones. Evans (1977) delineated the anaerobic decomposition of the benzene nucleus under three different sets of biological conditions. The three conditions are: anaerobic photometabolism of benzoate by Athiohodaceae, anaerobic metabolism of dichlorophenol, giving rise to quinolines. Quinolines were observed in the presence of fungal phenoloxidase in soil (Liu et al., 1981, Rosazza 1982).

Figure 22 (plot 30) shows an increase in polar compounds from points F to G, whereas there was no increase during the same time period in plot 35 (Fig. 23). During

the above time period, when an increase in polar compounds was seen in plot 30 phenol, 2 nitrophenol and pentachlorophenol, as well as benzene, nitrobenzene, and isophorone (Table 32), were detected in the soil matrix. This is reported in the fate of priority pollutants section of this study on 9/10/82, which corresponds to point F in Figure 22. The above compounds would increase the concentration of polar compounds. The characterization of priority pollutants at point G on 9/26/82 indicated the absence of phenolic compounds or benzene related compounds. The increase in polar compounds may be due to the formation of quinolines, as observed by Liu et al., (1981).

Nonenzymatic transformation of aromatic and phenolic compounds into polar compounds is also possible, due to the alteration of the physico-chemical environment by variations of pH, temperature, redox potentials and other factors in the formation of Xenobiotic compounds (Rosazza). Enzymatic conversion of organic sulfur compounds to sulfoxides in sterile soils were observed (Chin et al., 1970, Rosazza 1982). Sulfoxidation of carboxin by the fungus Utilago mayolis was observed in the soil by Lyr et al., (Rosazza 1982). Therefore, formation of polar compounds in the soil can be accounted for.

Based on the above results, the losses of the individual fractions were calculated. The results are tab-

ulated in Table 20. The loss of fractions during the first phase was greater than during the second phase. The relative magnitudes of the individual fraction losses were as follows:

1st phase: Saturates > Aromatics > Asphaltenes > Polar Compounds

2nd phase: Aromatics > Polar Compounds > Asphaltenes > Saturates

Table 20 Percent Losses of Oily Fractions

Plot #	Asphaltenes		Saturates		Aromatics		Polar Compounds	
	1	2	1	2	1	2	1	2
30	56.3	50.0	94.8	39.1	77.3	62.3	32.1	48.3
35	42.1	22.2	93.4	6.2	75.7	45.4	27.5	35.0
Mean	49.2	36.1	94.1	22.7	76.5	53.9	29.8	41.7

Analysis of Figures 16 through 23 shows that degradation of fractions was the highest from points E to H and J to K. The same phenomenon was observed for the total oil content. During winter months, the land treatment system acted as a storage unit with minimal degradation.

First order rate coefficients were computed for all fractions. The rate coefficients are presented in Table 21. The magnitudes of the rate coefficients for both phases are as follows:

Asphaltenes > Saturates > Polar Compounds > Aromatics

Asphaltenes showed a greater rate constant because as the asphaltenes degraded, other fractions were formed, hence, a greater net loss rate for asphaltenes. Whereas,

Table 21 Rate Coefficient for Oily Fractions Degradation

Plot #	Asphaltenes		Saturates		Aromatics		Polar Compounds	
	1	2	1	2	1	2	1	2
30	0.031	0.016	0.017	0.0114	0.0059	0.0097	-	0.013
35	0.026	0.011	0.014	0.0104	0.004	0.0086	0.0055	0.0104
Mean	0.0295	0.0135	0.0155	0.0124	0.00495	0.00915	0.0055	0.0117

the other fractions showed lower net loss rates, thereby reflecting a lower rate constant due to the degradation of asphaltnes. The pentane insoluble compounds (referred to as asphaltenes) built up during anoxic conditions were probably carboxylic acids, ketones, esters, aldehydes and alcohols (Walker et al., 1976). Therefore, as soon as the plots were tilled after the anoxic period, there was an immediate loss of the compounds, which were readily amenable to degradation under aerobic conditions, as shown by sharp drops in asphaltenes from G to H and J to K in Figures 16 and 17.

SUMMARY OF OIL CONTENT AND FRACTIONATION STUDY

The above results of oil content and fractionation show that oil and the associated fractions degraded with time. The degradation of oil and fractions occurred predominantly in the summer and fall months. An inhibition period was observed during winter months, when there was no appreciable degradation observed for oil content -

even though the individual fractions showed increases and decreases. During this period saturates, asphaltenes and polar compounds showed increases which were probably due to the anaerobic decomposition of oil. Aromatics were found to degrade even during winter months. A contribution of the degradation of aromatics to the remaining fractions as intermediate compounds is possible. Asphaltenes and polar compounds were found to degrade with time. This is contrary to the studies reported in the literature.

The mean oil losses calculated for this entire study was found to be in agreement with that reported in the literature (Table 15). The loss of fractions presented in Table 14 ranged from 58% to 89% for plot 30 and 36% to 81% for plot 35. The mean rate coefficients calculated on the basis of the above losses were found to be similar for fractions and oil content.

FATE OF PRIORITY POLLUTANTS

The fate of priority pollutants was studied in two steps. The first step involved the development of an identification and quantification technique (computer program) for the GC/MS/DS system. The second step involved the characterization of priority pollutants present in the refinery waste under study and following the fate of the priority pollutants characterized. There-

fore, the study will be presented as two sub-divisions.

Comparison of Identification and Quantification Techniques in GC/MS/DS

The GC/MS system used for identification and quantification of priority pollutants was not equipped with identification and quantification software; therefore, a computer program was developed called the IQ program. The IQ program was developed conforming to the three EPA criteria discussed earlier in this study. In order to compare the performance of the IQ method, programs were developed for McLafferty's (PBMQ) and Biemann's (HIBE) method of identification and quantification. The PBMQ and HIBE methods did not follow EPA criteria. The following section deals with the comparative study of the above three methods using eight standard compounds.

Three factors were analyzed for the comparison. The time taken for analysis of data, the reliability of peak matching and the spectrum numbers (peaks) identified were compared. The results of the above analyses are presented in Tables 22 through 28.

The results of the searching and printing times for all three methods are presented in Tables 22, 23, and 24. Comparison of the times showed that the IQ method was fastest of the three (Table 29). The reason for the above fact is that the PBMQ and the HIBE method go through complex algorithms (as discussed in the litera-

Table 22 Results of Test Run on IQ Program

Sample No.	Conc. of Standards	Volume Injected (µl)	Amount Injected (ng)	Time for Reading File	Time for Printing & Copying
DC1	200 ng/µl	1.2	240.0	45 sec.	5 min.
DC2	200 ng/µl	2.0	400.0	44 sec.	5 min.
DC3	200 ng/µl	0.5	100.0	45 sec.	5 min.
DC4	28 ng/µl	2.0	56.0	43 sec.	5 min.
DC5	28 ng/µl	0.5	14.0	41 sec.	5 min.
DC6	28 ng/µl	0.2	5.6	41 sec.	5 min.

No. of compounds in std. (including d_{10}anthracene) = 8 compounds

Table 23 Results of Test Run on PBMQ Program

Sample No.	Conc. of Standards	Amount Injected (µl)	Conc.in Amount Injected	Time for Reading File	Time for Printing & Copying
DC1	200 ng/µl	1.2	240 ng	79 sec.	7 min/30 sec
DC2	200 ng/µl	2.0	400 ng	65 sec.	7 min.
DC3	200 ng/µl	0.5	100 ng	56 sec.	7 min.
DC4	28 ng/µl	2.0	56 ng	56 sec.	7 min.
DC5	28 ng/µl	0.5	16 ng	56 sec.	7 min.
DC6	28 ng/µl	0.2	5.6 ng	56 sec.	7 min.

No. of compounds including d_{10}anthracene = 8 compounds

Table 24 Results of Test Run on HIBE Program

Sample No.	Conc. of Standards	Amount Injected (µl)	Conc.in Amount Injected	Time for Reading File	Time for Printing Results
DC1	200 ng/µl	1.2	240 ng	83 sec.	6 min.
DC2	200 ng/µl	2.0	400 ng	58 sec.	6 min/2 sec.
DC3	200 ng/µl	0.5	100 ng	53 sec.	6 min.
DC4	28 ng/µl	2.0	56 ng	53 sec.	6 min/3 sec.
DC5	28 ng/µl	0.5	14 ng	53 sec.	6 min.
DC6	28 ng/µl	0.2	5.6 ng	53 sec.	6 min.

No. of compounds including d_{10}anthracene = 8 compounds

Table 25 Peak Matching Capacity for IQ Program

		Matching Capacity					
No.	Name of Compounds	DC1	DC2	DC3	DC4	DC5	DC6
1	d_{10}-Anthracene	CM	CM	CM	CM	CM	CM
2	1,2-Dichlorobenzene	CM	CM	CM	CM	NM	NM
3	Napthalene	CM	CM	CM	CM	NM	NM
4	Hexachlorocyclo-pentadiene	NM	NM	NM	NM	NM	NM
5	Fluorene	CM	CM	CM	CM	CM	NM
6	Pyrene	CM	CM	CM	CM	CM	NM
7	Bis(2-ethylhexyl)-phthalate	CM	CM	CM	CM	NM	NM
8	Benzo(B)fluoranthene	CM	CM	CM	CM	NM	NM

Note: CM = Correct Match; NM = No Match

Table 26 Peak Matching Capacity for PBMQ Program

No.	Name of Compounds	Matching Capacity DC1	DC2	DC3	DC4	DC5	DC6
1	d_{10}-Anthracene	CM	CM	CM	CM	CM	CM
2	1,2-Dichlorobenzene	CM	CM	CM	CM	NM	NM
3	Napthalene	CM	CM	CM	CM	CM	CM
4	Hexachlorocyclo-pentadiene	NM	NM	NM	NM	NM	NM
5	Fluorene	CM	CM	CM	CM	CM	CM
6	Pyrene	CM	CM	CM	CM	CM	CM
7	Bis(2-ethylhexyl)-phthalate	CM	CM	CM	CM	CM	CM
8	Benzo(B)fluoranthene	CM	CM	CM	CM	NM	NM

Note: CM = Correct Match; NM = No Match

Table 27 Peak Matching Capacity for HIBE Program

No.	Name of Compounds	Matching Capacity DC1	DC2	DC3	DC4	DC5	DC6
1	d_{10}-Anthracene	CM	CM	CM	CM	CM	CM
2	1,2-Dichlorobenzene	CM	CM	CM	CM	NM	NM
3	Napthalene	CM	CM	CM	CM	CM	CM
4	Hexachlorocyclo-pentadiene	NM	NM	NM	NM	NM	NM
5	Fluorene	CM	CM	CM	CM	CM	CM
6	Pyrene	CM	CM	CM	CM	CM	NM
7	Bis(2-ethylhexyl)-phthalate	CM	CM	CM	CM	CM	CM
8	Benzo(B)fluoranthene	CM	CM	CM	CM	NM	NM

Note: CM = Correct Match; NM = No Match

Table 28 Comparison of Spectrum Numbers for IQ, PBMQ and HIBE

Name of Compounds	DC1			DC2			DC3			DC4			DC5			DC6		
	IQ	PBMQ	HIBE	IQ	PBMQ	HIBE	IQ	PBMQ	HIBE	IQ	PBMQ	HIBE	IQ	PBMQ	HIBE	IQ	PBMQ	HIBE
d_{10}anthracene	649	651	649	558	556	556	557	577	557	557	577	557	558	558	558	558	558	558
1,2-dichloro-benzene	178	178	179	79	79	79	79	79	79	79	79	79	51	77	77	51	99	74
Napthalene	267	267	268	170	167	167	169	169	168	169	169	170	154	168	168	154	168	168
Hexachloroclyco-pentadine	349	363	363	252	267	267	252	266	266	252	251	251	252	247	276	252	252	276
Fluorene	526	526	526	432	431	431	431	431	431	431	432	432	432	432	432	432	432	432
Pyrene	829	830	830	739	739	739	739	739	739	738	739	739	739	740	740	721	740	732
Bis(2-ethylhexly) phthalate	1001	1000	1000	912	911	911	911	912	912	911	912	912	875	913	913	875	912	912
Benzo(b) fluoranthene	1126	1127	1127	1038	1039	1039	1039	1040	1040	1040	1040	1040	1009	1054	1018	1009	1044	1030

ture review) in the identification of a compound. The search times for IQ, PBMQ and HIBE are 5.4 secs, and 7.67 secs and 7.35 secs per compound.

A comparison of the peak matching capacity of each method was performed. Correct matches were obtained for d_{10}-anthracene for all concentrations in all three searches. Correct matches were obtained for all three methods from DC1 to DC4 (DC1 through DC6 are sample numbers). In DC5 the IQ method did not yield correct matches for five compounds. In DC6 no matches were obtained for the IQ method; however, in the case of PBMQ and HIBE methods, a few matches were obtained as shown in Tables 26 and 27. The reason is that the IQ method will not yield a match if anyone of the criteria are not met, whereas the PBMQ and HIBE methods will. The disadvantage of the PBMQ and HIBE methods is that they will give rise to false positives (identification of a stray compound as the one in question) in complex spectra. Recently, Bruce Colby (1984) also concluded that the PBMQ method was inefficient due to identification of false positives. Therefore, the mass spectra must be inspected before acceptance of the match retrieved by the data manipulation system.

A comparison of the spectrum retrieved for a correct match was performed. It was found that all three methods yielded the same spectrum numbers when correct matches

were obtained, as shown in Table 28.

Table 29 shows the comparison of the above three methods. Based on these results the IQ method was found to be reliable, to follow the EPA protocol and to be faster than the HIBE and PBMQ methods.

Table 29 Comparison of IQ, PBMQ and HIBE Methods of Identification and Quantification

Method	Time Taken	Reliability (Yes/No)	Comments
IQ	5.4 secs/compound	Yes	Follows EPA protocol
PBMQ	7.67 secs/compound	Yes	Does not follow EPA protocol and leads to false positives
HIBE	7.35 secs/compound	Yes	Does not follow EPA protocol

Characterization of Priority Pollutants

This section deals with the characterization and the fate of priority pollutants due to the land treatment of oily sludges. Priority pollutants were monitored with time to determine the extent of production degradation, leaching and formation in the soil matrix. Samples were collected from the zone of incorporation and the unsaturated zone.

Priority pollutants found in the sludges (batches 1

and 2) are presented in Tables 30 and 31. Analysis of this data showed that the concentrations were at the parts per billion level. The results of priority pollutants monitored during this study are presented in Tables 32 and 33. Concentrations varied significantly from one sample to another in the same plot.

Due to the variations in concentrations of the priority pollutants, a variation analysis study was performed to determine the reason for variation. The sampling and sample analysis procedures were the same as described earlier. Four extractions were made from a single sample. Three aliquots were injected into the GC/MS from a single extract and three injections were made from the other three extracts.

Initially the variations of aliquots taken from a single sample bag were studied using three individual extracts injected into the GC/MS. Five peaks were chosen from the chromatogram. The total ion abundances of the peaks are presented in Table 34. A statistical analysis was performed on the data in this table and the coefficient of variation ranged from 32% to 72%.

The above data shows significant variations for three samples extracted from a single sample bag. Recent EPA performance evaluation data (30) also show variations of recoveries of surrogate standards spiked in a uniform sample matrix. The variations range from 15% to 108% de-

Table 30 Priority Pollutants Present in the Oily Residues, Batch I

Names of Compounds	Range of Conc. in ppb
Napthalene	1.61 - 136.61
N-nitrosodiphenylamine	<0.01 - 0.075
Isophorone	<0.01 - 39.76
Fluorene	<0.01 - 1.64
Phenanthorene	<0.01 - 0.896
Anthracene	<0.01 - 0.574
Pyrene	<0.01 - 0.056
Chrysene	<0.01
Benzo(A)anthracene	<0.01
2,4-Dinitrotoluene	0.087 - 630.66
Trichloroethylene	0.047 - 137.70
Benzene	<0.01 - 16.83
Ethylbenzene	7.51 - 90.9

Table 31 Priority Pollutants Present in the Oily Residue, Batch II

Compound Present	Conc. in ppb
Toluene	3.53
Ethylbenzene	0.37
Isophorone	<0.01

Table 32 Priority Pollutants Present at Different Times for Plot No. 30

Compounds	Concentration Range in ppb				
	4/7/82	9/10/82	9/26/82	11/8/82	12/20/82-6/9/83
	Set I	Set II	Set III	Set IV	Set V - VI
Isophorone	10.74-68.0	0.064-1.299	ND	ND	
Fluorene	10.21-30.35	ND	ND	ND	
Phenanthrene	0.088-126.4	ND	ND	ND	
Anthracene	<0.01-0.021	ND	ND	ND	None Present
Trichloroethylene	1.98-2.67	ND	0.514-0.762	ND	
Benzene	<0.01	<0.01	ND	<0.01	
Ethylbenzene	<0.01	ND	ND	ND	
Nitrobenzene	ND	0.019-0.038	ND	ND	
Phenol	ND	<0.01	ND	ND	
2-Nitrophenol	ND	<0.01	ND	ND	
Pentachlorophenol	ND	<0.01	ND	ND	
Pyrene	ND	<0.01	ND	ND	

ND denotes non-detectable

Table 33 Priority Pollutants Present at Different Times for Plot No. 35

Compounds	Concentration Range in ppb			
	6/7/82	9/10/82	9/26/82	11/8/82 - 6/9/83
	Set I	Set II	Set III	Set IV - V
Isophorone	0.728-14.7	<0.01	ND	
Phenanthrene	<0.01-522.98	ND	ND	
Anthracene	<0.01-0.267	ND	ND	None Present
Fluoranthene	<0.01-0.065	ND	ND	
2,4-Dinitro-toluene	0.41-3.62	ND	1.572	
Benzene	<0.01	ND	ND	
Phenol	ND	<0.01	ND	
Pyrene	ND	ND	<0.01	

ND denotes non-detectable

Table 34 Variation of 3 Samples from a Single Bag of Samples

Plot #	Retention Time	Total Ion Abundances Sample			Coeff. of Variation %
		#1	#2	#3	
1	9.62	4626	2948	9478	60
2	10.00	1313	818	2152	47
3	11.18	7072	1257	9800	72
4	12.18	3092	1487	1913	38
5	13.56	13470	9064	7319	32

Amount of sample injected = 2 microliters in all cases by solvent flush technique with methanol.

pending on the compound recovered.

Next, the variation due to three injections from a single extract was studied. Three peaks were chosen from the chromatogram. The total ion abundances of the three peaks are presented in Table 35. Analysis of the data showed minimal variation. The coefficient of variation was between 0.68 to 1.05 .

A study of the variation of the priority pollutants across the plot was performed. Three samples taken from a plot were analyzed for priority pollutants. The data is presented in Table 36. The coefficient of variation ranged from 92% to 148%. Variations are inherent in the sampling and sample preparation as evidenced by the fact that the variations, in the results, were greater for

Table 35 Analyses of 3 Injections from a Single Extract

Peak #	Retention Time	Total Ion Abundances Injection			Coeff. of
		#1	#2	#3	Variation %
1	10.82	1689	1630	1648	.68
2	11.56	4389	4326	4127	.96
3	13.0	3101	3378	3065	1.05

analyses performed on three aliquots from a single, well mixed sample than that for repeated analyses from a single extract. Variations between samples were also observed.

Further variations as to the presence or absence of compounds taken from a single plot were studied. Table 37 shows the presence or absence of a compound from one sample to another. Among the three samples there were five compounds present. In sample number 1 only three of the five were present; in sample number 2 none were present; and in sample number 3 four compounds were present. The above data indicates the variation even in the presence or absence of compounds apart from variations in the total ion abundances. Despite variations in the data, priority pollutants were not detected after a period of 426 days, which indicates that priority pollutants were degraded or lost as volatiles.

Analysis of the priority pollutants data showed that phenolic compounds were synthesized. Initially, no phen-

Table 36 Variation of Abundances in 3 Samples Taken from a Single Plot

Sample #	Abundances			
	Isophorone	Benzene	Anthracene	Chloroform
1	1.926×10^7	1.555×10^5	2.561×10^6	1.041×10^6
2	2.358×10^8	7.9×10^5	3.584×10^7	2.067×10^7
3	9.910×10^6	2.039×10^5	1.236×10^6	-
Coeff. of Variation %	144.7	92.18	148.24	-

Table 37 Variation in the Presence or Absence of Compounds in 3 Samples Taken from a Plot.

Sample #	Name of Compounds				
	Naphthalene	Isophorone	Fluorene	Pyrene	Chrysene
1	P	A	A	P	P
2	A	A	A	A	A
3	P	P	P	P	A

P = Present
A = Absent

olics were found in the soils or sludges. On 9/10/82, phenolic compounds were detected. However, the samples on 9/26/82 did not contain any phenolic compounds. Stanlake and Finn studied the degradation of pentachlorophenols (PCP) and the bacterium involved in the degradation. In their study they found that no correlation existed between the degradation of PCP and the extent of initial bacterial growth. Degradation took place after one to two weeks. After the degradation of the initial load subsequent additions of PCP took only one to three days. The bacterium isolated was the genus Arthrobacter. Based on the above studies, disappearance of phenolics within sixteen days (as observed in the present study) is possible. Another possibility is that phenolics could combine with aromatics to form quinolines as discussed earlier.

Unsaturated zone was monitored for priority pollutants. Core samples and soil moisture samples were collected to study the migration of priority pollutants through the soil matrix. The results of the unsaturated zone monitoring studies for organic pollutants are presented in Table 38. In April the initial sampling results showed that there were two priority pollutants present in plot 30 and seven in plot 35. The variation in the occurrence of priority pollutants is a result of the fact that they are only present in trace levels (ppb)

Table 38 Organics Found in the Unsaturated Zone

Plot No./ Date of Sampling	Depth	Compounds Present	Range of Conc. in ppb
30,	12-16"	Chloroform	<0.01 - 12.09
4/7/82		Trichloroethylene	<0.01 - 3.48
35,	12-16"	Chloroform	<0.01 - 103.01
4/7/82		Trichloroethylene	<0.01 - 98.97
		Benzene	<0.01 - 1.85×10^3
		Isophorone	<0.01 - 0.026
		Phenanthrene	<0.01 -
		Anthracene	<0.01 -
		Fluoranthene	<0.01 -
30,	36-42"	Chloroform	26.29 - 65.69
9/30/82	36-42"	Trichloroethylene	<0.01 - 11.02
	36-42"	Benzene	<0.01 -
35,	34-40"	Chloroform	0.552 - 57.34
9/30/82	34-40"	Trichloroethylene	<0.01 - 1.853
30, 35		None	
7/15/83		present	

and the variation in adsorptive capacity of priority pollutants on the soil particles, which depends on the uniformity of the soil and affinity for the compounds.

Subsequent sampling in October showed that there were only three priority pollutants present. The specific concentrations of the pollutants are given in Table 38. The sampling on 7/15/83 indicated the absence of priority pollutants in the unsaturated zone. Samples from soil moisture samplers did not contain priority pollutants.

From the above results it is evident that no significant migration of organics below the zone of incorporation had occurred. No priority pollutants were detected at the end of this study. Degradation took place even though variations were observed.

CHAPTER 7

CONCLUSIONS

The major goals of this study were to develop a method for the identification and quantification of priority pollutants; to develop methods for sampling, sample preparation and for oil content analysis; to study the degradation of oil and oil fractions; and to study the fate of priority pollutants. In order to fulfill these goals, the above studies were conducted. The conclusions of the studies are as follows:

1. The results of the GC/MS/DS show that the IQ program was as reliable and faster than other methods. The IQ program followed the EPA protocol, whereas the PBMQ and HIBE methods did not.
2. The oil content analysis procedure, sample preparation procedures and sampling techniques developed in this study yielded consistent results.
3. First order rate constants for the degradation of oily residues and oil fractions were similar.
4. Loss of oily residues and oily fractions was highest during the summer and fall months.
5. During the winter months there was minimal degrada-

tion of oil, whereas the individual fractions showed changes.

6. No significant migration of oily residues and priority pollutants occurred.
7. Asphaltenes, saturates and polar compounds were found to increase during the winter period, due to production of the fractions as anaerobic decomposition products.
8. Initial concentrations of priority pollutants were in the ppb range.
9. Concentrations of priority pollutants varied significantly from one sample to another across the plot.
10. The variation in concentration of priority pollutants was inherent to the method of analysis and a result of the non-uniformity of the oil matrix across the plot.
11. Initially, no phenolic compounds were detected in the sludges and background soils. However, after a period of time, phenolics were detected; this indicates the formation of phenolics in the soil matrix.
12. Priority pollutants degraded with time, and none were detected at the end of this study.

CHAPTER 8

RECOMMENDATIONS FOR FUTURE STUDY

1. All analytical procedures should be adapted to the project even though standard EPA procedures are available.
2. Further investigation is necessary in the area of soil structural changes to understand the influences of oily residues on soil structure.
3. HPLC should be used in fractionating the oil in order to minimize errors, speed up the analysis and avoid exposure of researchers to benzene in large quantities.
4. Adapt the jet fuel analysis (C_4-C_{20}) procedure as described in ASTM D2857 to study the degradation or formation of hydrocarbons.
5. Develop individual priority pollutant analysis procedures for specific sample matrices.
6. Develop methods to minimize variations in concentrations of priority pollutants.
7. Develop a method for combining the phenolic extract and base neutral extract into a single extract for priority pollutant analysis. This would reduce the

time of analysis and would be more cost effective.

8. Perform column studies (using soil columns from site) in the laboratory to determine the fate of priority pollutants.
9. Land treatment study should be conducted for a longer period of time to insure equilibrium conditions and develop rate coefficients of oily residues and oily fractions for equilbrium conditions.

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APPENDIX A

OIL CONTENT ANALYSIS

AIM: To recover the total oil from a given sample.

APPARATUS AND MATERIALS REQUIRED: Soxhlet extraction apparatus, steam bath oven, a balance, thimbles to fit the Soxhlet extraction apparatus, beakers, glass rods, methylene chloride, (Reagent grade) glass beads, and aluminum weighing dishes.

PROCEDURE:

1. A tared thimble is weighed.
2. 20 gms of the given sample is weighed into the thimble.
3. 225 mls of methylene chloride is poured into a clean, dry flat bottomed flask.
4. Glass beads are added to the flask.
5. The thimble with the sample is placed in the Soxhlet extraction apparatus.
6. The heating unit is turned on after the cooling water is turned on.
7. The sample is extracted for 4 hours with methylene chloride.
8. At the end of 4 hours the heating unit is turned off and the flask is allowed to cool.
9. The thimble is taken out after the solvent has been drained and dried in an oven at 105°C.

10. The solvent is evaporated on a steam bath until a volume of 10-15 mls remain in the flask.
11. The 10-15 ml of solvent is tranferred to a pre-weighed aluminum weighing dish, by pouring over a clean glass rod, the flask and the glass rod are washed with 2-3 ml portions of methylene chloride and allowed to evaporate at room temperature.
12. Periodic stirring may be required to break the film formed on the surface.
13. After evaporation the aluminum dish with the oil is weighed.
14. The dried thimble is also weighed and the oil and moisture contents are calculated.

$$\% \text{ OIL CONTENT} = \frac{\text{Wt. of oil} * 100}{\text{Wt. of dry soil + thimble} - \text{Wt. of thimble}}$$

NOTE: For water samples the extraction is done using a separatory funnel and the rest of the procedure is the same as above.

All glassware are washed with soap solution, rinsed off with distilled water and dried in an oven before analysis.

APPENDIX B

RAW FRACTIONATION AND OIL CONTENT DATA - PLOTS 30 and 35

Plot	Elapsed Day	% Oil In Soil	% Asph. In Oil	% Sat. In Oil	% Arom. In Oil	% Polar In Oil
30	385	4.39	4.68	48.46	30.74	19.12
	385	4.91	4.10	43.27	30.74	16.85
	385	4.19	4.88	48.30	30.74	24.34
	401	3.18	5.81	40.45	28.20	25.43
	401	3.14	6.11	40.32	28.20	24.83
	401	3.13	5.79	41.50	28.20	25.12
	444	2.90	8.85	30.63	27.33	33.20
	444	2.75	8.64	29.94	26.85	34.57
	444	2.90	8.32	36.49	12.29	42.90
	486	1.91	3.90	23.84	36.72	35.54
	486	2.02	3.20	15.70	55.03	26.07
	486	1.88	5.71	19.45	33.70	41.15
	598	4.26	5.34	33.40	24.66	36.59
	598	5.60	5.66	30.59	27.20	36.55
	598	9.47	5.15	30.92	27.27	36.66
	627	5.40	5.85	.	.	.
	627	5.15	6.03	.	.	.
	627	4.75	7.56	.	.	.
	657	2.57	4.00	42.61	13.66	39.72
	657	4.51	5.43	35.33	28.15	31.09
	657	2.49	4.61	31.46	31.19	.
35	385	5.13	6.94	48.51	20.59	23.97
	385	5.36	5.70	35.11	12.52	44.67
	385	5.63	4.48	19.28	35.95	40.29
	401	4.15	.	44.21	.	36.21
	401	4.33	.	43.22	.	37.49
	401	4.63	.	43.22	.	37.49
	444	3.84	8.26	30.69	24.97	36.08
	444	3.82	8.32	24.67	30.32	38.69
	444	3.95	9.76	28.83	23.77	37.64
	486	2.56	4.37	20.27	36.72	38.15
	486	2.54	6.18	20.34	35.32	4.92
	486	2.33	4.89	22.90	35.05	19.07
	598	8.42	7.75	33.16	21.27	37.82
	598	6.07	5.65	41.72	19.68	32.95
	598	8.98	6.69	36.40	19.69	21.10
	627	6.97	6.49	.	.	.
	627	6.35	6.84	.	.	.
	627	6.23	7.43	.	.	.
	657	5.11	4.90	38.07	31.43	25.59
	657	3.42	5.36	44.62	11.40	38.29
	657	5.38	5.87	12.68	31.43	25.59