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AN INVESTIGATION OF THE PRESENCE AND MOBILITY OF POLLUTANTS AT SITES USED FOR LAND TREATMENT OF OILY RESIDUES

The University of Oklahoma PH.D. 1983

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AN INVESTIGATION OF THE PRESENCE AND MOBILITY OF POLLUTANTS AT SITES USED FOR LAND TREATMENT OF OILY RESIDUES

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AN INVESTIGATION OF THE PRESENCE AND MOBILITY

OF POLLUTANTS AT SITES USED FOR LAND

TREATMENT OF OILY RESIDUES

A DISSERTATION

APPROVED FOR THE DEPARTMENT OF

CIVIL ENGINEERING AND ENVIRONMENTAL SCIENCE

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ABSTRACT

The purpose of this study was to evaluate the conditions which exist at sites used for the land treatment of oily residues, after closure. Three sites, which had closed for different periods of time were selected and the site soil was analyzed for priority pollutants, and evaluated for the characteristic of Extraction Procedure (E.P.) Toxicity. Soil samples from the sites were also analyzed for oil content, pH, CEC, T.O.C., Cl^- and heavy metals. Soil pore water and deep core samples were analyzed for heavy metals, oil content and selected priority pollutants, to determine whether or not pollutants were reaching the unsaturated zone.

The results show that no appreciable degradation of the oil present at the sites took place over a 15 month period. The soil pore water contained Cl^- at concentrations from 12 mg/l to 5000 gm/l, Fe and Mn at concentrations from trace amounts to 12 mg/l, Zn and Ba at concentrations up to 5 mg/l. The E.P. Toxicity extract of the site soils did not contain any compounds above the allowed levels. Thus, the sites did not exhibit the characteristic of E.P. Toxicity. In addition there was

no correlation between the concentration of metals in the E.P. Extract and the concentration in the soil pore water, showing that the test does not model the leaching of metals under the conditions existing at these sites.

The results show that the priority pollutants present at these sites were primarily PNA's and phenolics, and that the metals and oil were generally immobilized in the top 25-50 cm of soil. However, some metals were mobilized and could present a pollution threat. Analysis of soil pore water and deep core samples indicated the presence of trace amounts of several organics in the unsaturated zone up to a depth of 150 cm. Further analysis of soil and water samples from the unsaturated zone below 150 cm is required to determine the extent to which organics are penetrating the unsaturated zone.

AN INVESTIGATION OF THE PRESENCE AND MOBILITY OF POLLUTANTS AT SITES USED FOR LAND TREATMENT OF OILY RESIDUES

CHAPTER 1

INTRODUCTION

Land treatment as a method of disposal of oily residues from oil refinery operations has become very popular in recent years. The technique has been in use for 15 to 20 years, and several studies have been performed to determine the fate of the oil and metals at active land treatment sites. However few studies have been carried out on the long-term effects on the site soil of land farming operations, or on monitoring the unsaturated zone at closed sites to see if a long-term threat to ground water exists at these sites. The purpose of this report is to describe a study carried out at three closed land treatment sites. The objective of this study was to:

(a) Identify priority pollutants present in the site soil.

(b) To evaluate the site soil for the characteristics of E.P. Toxicity, and to determine the effectiveness of the E.P. Toxicity procedure

for modelling the characteristics of site leachate.

(c) To determine the extent of vertical migration of pollutants.

To achieve these objectives land treatment sites which had been in use for a number of years were selected. Soil samples from depths 0-25 and 25-51 cm were analyzed for oil content, metals, T.O.C., C.O.D., pH, nutrients, chloride, cation exchange capacity, and selected organic compounds. The unsaturated zones at the sites from 51-152 cm were also sampled, and analyzed for oil content, metals and selected organic compounds. The soil pore water in the unsaturated zone was also sampled using soil pore water samplers, and the samples analyzed for oil content, metals, T.O.C., C.O.D. and selected organics.

The 0-25 and 25-51 cm depths were chosen, because land treatment sites are tilled, and the till zone usually extends to a depth of about 25 cm. Since this depth is completely mixed during tilling, it was felt that sampling shallower depths would be unproductive. The depth 25-51 cm was chosen since preliminary sampling at these sites indicated the presence of oil in some areas up to this depth.

Samples of soil pore water were collected as a part of the unsaturated zone monitoring program, to see whether any pollutants were passing through the unsatur-

ated zone, and if so, in what quantities.

Samples of the 0-25 cm and 25-51 cm zones were analyzed for oil content over the duration of the project, in an attempt to determine rates of degradation. In addition a part of each site was tilled, to see if this enhanced the rate of degradation when compared to the untilled section of the site.

The major thrust in the analysis of the site soil and soil pore water for priority pollutants, was to identify qualitatively the compounds present. Quantitative evaluation was beyond the scope of this project, although concentrations of the compounds identified were calculated, to give an idea of the order of magnitude of the concentrations of these compounds.

The other parameters measured are all important as indicators of the amount of oil present, and the potential for mobilization of pollutants, especially metals.

Soil Samples from the sites were subjected to the E.P. Toxicity procedure, and the extract analyzed for metals and selected priority pollutants. The results were used to classify the site with regards to the characteristic of E.P. Toxicity and were also compared with the results obtained from soil pore water monitoring. The latter comparison was made to determine whether the E.P. Toxicity procedure modelled actual leaching in the soil.

The site soil was also evaluated for changes in permeability, soil structure, soil texture and cation exchange capacity.

CHAPTER 2

LITERATURE REVIEW

The petroleum refining industry generates large amounts of waste each year, a sizeable proportion of which is classified as hazardous. Galloway (1979) reported on an EPA survey which placed the amount of hydrocarbons in refinery solid wastes at 169,465 metric tons per year.

The individual process streams which contribute to this quantity are listed below (Rosenberg et al., 1976).

1. Crude tank bottoms - solid sediment from incoming crude oil, which has accumulated at the bottom of the crude oil storage tanks.
2. Leaded or non-leaded tank bottoms - solids which settle to the bottoms of product tanks.
3. API separator sludge - solids which settle in the API separator during primary wastewater treatment.
4. Neutralized HF alkylation sludge - alkylation sludge produced by both the sulfuric acid and hydrofluoric acid alkylation processes.
5. Kerosene filter clays and lube oil filter clays

- clays used to remove color bodies, chemical treatment residues, and traces of moisture from product streams.

6. Once-through cooling water sludge - sludge from primary settling tanks used for cooling water.
7. Dissolved Air Flotation (DAF) float - generated when dissolved air flotation is used to remove oil and solids from wastewater streams.
8. Slop oil emulsion solids - solid fraction of oil skimmed from API separators.
9. Spent lime from boiler feedwater treatment.
10. Cooling tower sludge - sludge which settles out in the cooling tower basin.
11. Exchanger bundle cleaning sludge.
12. Waste bio sludge - excess sludge from biological treatment of refinery aqueous waste streams.
13. Storm water silt - silt which collects in the stormwater settling basins.
14. Fluid Catalytic Cracker (FCC) catalyst fines - generated when catalyst is regenerated by burning off coke produced during usage of the catalyst. Collected by electrostatic precipitators or similar pollution control devices.
15. Coke fines.
16. Spent catalysts.

17. Chemical precipitation sludge - produced when chemical coagulation is used to remove suspended matter from aqueous waste streams.
18. Vacuum filter or centrifuge cake.
19. Silica gel - used to remove water from instrument air.

DAF float, slop oil emulsion solids, heat exchanger bundle cleaning sludge, API separator sludge and leaded tank bottoms are classified as hazardous by the Environmental Protection Agency (CRF Title 40, July 1982).

Table 2.1 lists the characteristics of some refinery solid wastes. The wastes with highest oil content are API separator sludge, DAF float, tank bottoms and vacuum filter sludges.

There are essentially three ways of disposing of these refinery solid wastes. These are landfilling, incineration and land treatment. Of these three, land treatment is rapidly becoming the most popular, because it is relatively inexpensive (Grove 1978), and is thought to be environmentally safe. Incineration is expensive, while landfilling does not treat the waste, but merely stores it in the ground, where it becomes a potential source of ground water contamination.

Disposal of oily residues by land treatment has been practiced for the last 15 to 20 years, but has become widely used only in the last 10 or so years. In

Table 2.1 Characteristics of Refinery Solids Wastes

Waste Type	Typical Composition, Percent: Oil or Hydrocarbon	Water	Volatile Solids	Inert Solids	Characteristics
API Separator Sludge	15	66	6	13	Fluid slurry of oil, water and sand
Tank Bottoms	48	40	4	8	Oil-water mixture
Chemical Treatment Sludge	5	90		5	Slightly viscous fluid
Air Flotation Froth	22	75		3	Thick, oily fluid
Precoat Vacuum Filter Sludges	22	29		49	Temperatures
Biological Treatment Sludges					
Raw	0	98	1.5	0.5	Water Consistency
Mechanically Thickened	0	94	4	2	Thick, but pumpable
Centrifuged	0	85	10	5	Viscous-peanut butter consistency
Vacuum Filtered	0	75	15	10	Wet crumbly solid
Screw Pressed	0	40	40		Intact, solid cake
Water Treatment Sludge	0	95		5	Pumpable fluid, sometimes gelatinous

Cross, F.L. and J.R. Lawson, "A New Petroleum Refinery". American Institute of Chemical Engineering Symposium Series, Vol. 70, No. 136, P. 812.

this method, the wastes are applied to the soil, tilled or disced into the top 15 to 20 centimeters (0 to 6 inches), nutrients added, and the residues allowed to biodegrade.

Several researchers have investigated land treatment of oily residues in the last few years. These include Kincannon, 1972; Raymond, Hudson and Jamison, 1976; Cresswell, 1977; Huddleston and Meyers, 1978; Odur, 1978; Meyers and Huddleston, 1979; Huddleston, 1979; and Lewis. The results of these research projects have been cited extensively in the literature, and will not be reviewed extensively here. The general conclusion drawn from this body of work has been that land treatment is an environmentally sound and effective way to dispose of oily residues.

Cresswell (1977) identified the primary factors affecting the degradation of oily residues as:

(1) Petroleum composition

(2) Temperature

(3) Nutrients

(4) Oxygen availability

(5) Water content of soil

(6) Soil pH

These conclusions have been verified by several researchers.

Crude oil itself contains hundreds of organic com-

pounds, as well as trace amounts of many metals. Several of these organic compounds are classified as hazardous. Table 2.2 lists a number of toxic pollutants which have been identified in treated effluents from refineries (EPA, 1979). Table 2.3 lists the concentration range of several metals in refinery sludges, and compares this to the range in municipal sludges.

Metals, apart from V and Ni, occur in crude oil in trace amounts (Davis, 1967 and Valkovic, 1978). These metals are thought to be present as

(a) metalloporphyric chelates,

(b) transition metal complexes of tetradentate mixed ligands such as V, Ni, Fe, Cu, Co and Cr,

(c) organometallic compounds such as Hg, Sb and As,

(d) carboxyllic acid salts of the polar functional groups of resins, such as Mo, Zn, and Ge,

(e) colloidal minerals, such as silica and NaCl.

(Valkovic, 1978).

The high concentrations of some metals found in refinery sludges, such as Pb, are usually introduced as a result of the processing of the crude oil.

The land treatment process has to be capable of treating the hazardous constituents of oily residues, so that they do not pose an environmental threat. This is accomplished by immobilizing the metals in the soil, and by biodegradation of the organics.

Table 2.2 Toxic Pollutants Detected in Refinery Treatment Effluents

1. Organics

Benzene	bis(2-ethylhexyl)phthalate
1,2-dichloroethane	diethylphthalate
1,1,2,2-tetrachloroethane	benzo(a)anthracene
parachlorometacresol	benzo(a)pyrene
1,2-trans-dichloroethylene	chrysene
2,4-dimethylphenol	anthracene
ethylbenzene	benzo(g,h,i)perylene
fluoranthene	fluorene
methylene chloride	phenanthrene
dichlorobromomethane	pyrene
naphthalene	tetrachloroethylene
4-nitrophenol	toluene
phenol	trichloroethylene

2. Pesticides

None

3. Metals

antimony (total)	lead (total)
arsenic (total)	mercury (total)
chromium (total)	nickel (total)
beryllium (total)	selenium (total)
cadmium (total)	silver
copper (total)	thallium (total)
cyanide (total)	zinc (total)

4. Others (Asbestos, 4AAP Phenol)

None

Ref: EPA "Development Document for Effluent Limitations Guidelines and Standards for the Petroleum Refining Point Source Category", EPA 440/1-79/014-b, December 1979, Effluent Guidelines Division, E.P.A.

Table 2.3 Comparison of Heavy Metals in Sludges*

Metal	Range ppm in refinery oily solids†	Range, ppm in municipal solids
Arsenic	<1-294	3-30
Cadmium	<1-6	7-443
Chromium	<1-554	169-14,000
Copper	4-153	458-2,800
Mercury	<1-2	3-16
Nickel	<1-580	36-562
Lead	1-790	136-562
Selenium	<1-27	2-9
Vanadium	<1-455	15-92
Zinc	9-9,092	560-6,890

* All data on dry weight basis; all numbers rounded for simplicity.
† Jacobs Report, 1976.

It has been clearly established over the years, that several species of microorganisms are capable of degrading oil. Zobell (1972), reports that 200 species of bacteria, yeasts and filamentous fungi metabolize one or more kinds of hydrocarbons ranging from CH_4 to compounds with 40 or more carbons. Crow, Meyers and Ahearn (1974), also put the figure at around 200 different species. Extensive tests carried out with various microorganisms on hydrocarbon substrates, reveal Pseudomonas to be the dominant species capable of metabolizing hydrocarbons (Stearns, Ross and Morrison, 1977).

Wardley-Smith (1983) reported that the microorganisms most commonly isolated which are involved in hydrocarbon breakdown are Gram negative rods such as Pseudomonads and Alcaligenes. Other genera isolated are Micrococci Corynebacteria, Mycobacteria, Nocardia, Candida and Penicillium.

Although large numbers of species of microorganisms which degrade hydrocarbons have been identified, the pathways utilized in the degradation of oily residues by mixed cultures have not. Cansfield and Racz (1978) reported degradation of all components of hydrocarbon residues from crude oil storage tanks. Fifty percent of the total residues applied were degraded in 833 days. Saturates were degraded 54.6 percent, monoaromatics 50.0 percent, diaromatics 57.1 percent, polyaromatic and polar

compounds 44.4 percent, and high molecular weight material such as Asphaltenes was only degraded 11.1 percent. They reported that the alkanes degraded to low levels in the first 106 days. Cansfield and Racz found that the polar fraction increased and then decreased, and speculated that degradation of all fractions would occur through the formation of polar compounds.

Davis (1967) also reported work which showed that paraffinic hydrocarbons (alkanes) in the medium molecular weight range were oxidized more readily than either the low molecular weight paraffins, or the heavy paraffinic fractions. Aromatic fractions were more difficult to degrade than paraffins.

Most of the data produced by land treatment studies has focused on short-term effects. Few researchers have evaluated the potential for long-term impacts on the environment. These long term impacts need to be addressed in view of the fact that there is a buildup of heavy metals in the soil during land treatment. Fuller (1977) reported that under anaerobic conditions the mobility of several heavy metals (As, Cr, Fe, Cu, Zn) is enhanced. (Anaerobic conditions can and do occur at land treatment sites, particularly under conditions of high soil moisture content, when leaching is most likely to occur).

Hahne and Kroontje (1973) reported that in the

presence of chloride ion, the solubility of Cd, Zn, Pb, and Hg is increased even at a pH as high as 9. They indicated that at a pH of 9 soluble chloride complexes can be found at ion concentrations of 354 to 28 ppm. High chloride ion concentrations can be present at land treatment sites because of the occurrence of brines with crude oil and the high chloride ion content of some of the wastes which result from refinery operations.

Soils used for the disposal of oily sludges may contain a number of heavy metals which are potentially toxic to the environment. Contamination of ground water by heavy metals is believed to be of minimal concern if adequate soil pH is maintained at a land treatment site. Most metals are immobilized when the soil pH is greater than 6.5. The leaching of metals is therefore not of major concern at treatment sites with proper pH control (Dibble and Bartha 1979, Francsen 1980, Huddleston 1979, Lewis).

Leeper (1978) believes that pH is the single most important aspect of the reaction between heavy metals and soils. Soil treated with sludges containing heavy metals should be medium to fine textured, have a pH above 6.5 and contain 3-7% organic matter with a CEC of at least 14 in order to be considered acceptable for the retention of metals (Huddleston 1979, Leeper 1978, Loehr 1979).

Hydrocarbon Processing (1980) reported that

"virtually all published information on landfarming indicates that there is little migration of contaminants below the top 30 centimeters (12 inches) of soil". The EPA maximum allowable depth for the movement of metals and other contaminants is 91 centimeters (36 inches). Little work has been done to date on the leaching of metals in soil containing oily wastes, although the movement of heavy metals in landfills or in soils amended with sewage sludge has been studied extensively (Schilesky 1979).

Raymond et al. (1976) conducted a land treatment study in which oil degradation was monitored over a one year period. The movement of lead, which was the metal of highest concentration in the oil, was examined and no evidence was found that the nitric acid-soluble form had leached through the soil.

Dibble and Bartha (1979) found hydrocarbons did not leach below a depth at which oil sludge was mixed with sandy soil. Based on Raymond et al.'s studies, Dibble and Bartha concluded that heavy metal residues from oil sludges would display low mobility in limed soil.

The possibility of heavy metals leaching through soil is great, if high pH levels are not maintained at land treatment sites. Heavy metals can be toxic, therefore suitable oily wastes for land treatment are those which do not contain extremely high metal concentrations

(Huddleston 1979).

Huddleston et al. (1982) reported in a study carried out at five closed refinery land treatment sites, that wastes had been degraded without appreciable migration of degradation products, and that metals in the waste remained in the waste application zone.

One problem which might arise from the disposal of oily residues by land treatment, is the movement of leachate through the unsaturated zone to the underlying ground water, resulting in contamination of the ground water. Thus, the unsaturated zone at a land treatment site needs to be monitored in order that any pollutant movement can be detected. Current EPA regulations require the use of monitoring wells, and the collection and analysis of soil core samples as a method of detecting pollutant movement. The EPA has also recommended the use of soil moisture samplers for sampling soil pore water in the unsaturated zone under active land treatment sites.

Soil moisture samplers using a porous ceramic cup have been used for many years for collecting soil pore water samples. Briggs and McCall first reported on the use of porous ceramic cups in 1904, and since that time, their usage has increased considerably. However, with their increased usage, questions have arisen as to the validity of samples collected in this way.

Wagner (1962) used the porous ceramic cup and reported no adsorptive capacity of the cup for nitrate ions, but an appreciable adsorptive capacity of about 1 mg of N for NH_4^+ ions. Reeve and Doering (1965) used ceramic cups to collect soil water samples for salinity determinations. The values obtained from the sampler agreed with the values obtained by the conventional saturation method. They also found that the composition of the sample changed with time, but that consistent and reliable values for the composition of the soil solution were obtained when a vacuum in the range of 0 to 500 millibars was used to collect the sample.

Grover and Lamborn (1970) reported that ceramic cups contributed excessive amounts of Ca^{++}, Na^+ and K^+ to solutions drawn through them, and adsorbed phosphorus from solutions containing phosphorus. They found that leaching the cups with 1 N HCl reduced Na and K contamination, and the amount of phosphorus adsorbed, but appreciable amounts of calcium contamination still occurred. Wood (1973) also reported contamination of samples by Ca^{++}, Mg^{++}, Na^+, HCO_3^- and SiO_2. He minimized the problem by leaching the ceramic cups with 8 N HCl.

Zimmermann, Price and Montgomery (1978) reported loss of nutrients after filtration through porous ceramic cups used to sample sediment. The most significant losses occurred with NH_4^+ and phosphate ions. Levin and

Jackson (1977) also reported loss of NO_3-N when they used porous ceramic cups for sampling soil water. However, Johnson and Cartwright (1980) used soil moisture samplers with porous ceramic cups for sampling the unsaturated zone under landfills in Illinois. They found that samples taken with soil moisture samplers were representative of the surrounding leachate composition of major ions. They pointed out that while sample variability or bias of several milligrams per liter may be quite significant when the concentration of the ions of interest in the soil water is low, this is not the case when sampling highly contaminated leachate with high ionic concentrations.

England (1974) pointed out the following:

(1) Concentrations and composition of the soil solution are not homogeneous throughout its mass.

(2) Cations vary widely in the degree of dissociation from the surface of electronegative colloidal particles. Water drained from large pores at low suctions may have a different chemical composition from that extracted from micropores.

(3) Concentrations of various ions in a soil solution generally do not vary inversely with the soil water content. Dissolved quantities of some ions increase with increasing soil

moisture while quantities of other ions may decrease.

Hansen and Harris (1975), did extensive work on the use of porous ceramic samplers. They found that the rate of sample uptake was strongly influenced by cup uptake rate, plugging of the cup, sampler depth, and the type of vacuum system used. They also found that a number of factors affected the sample concentration as the sample was drawn through the ceramic cup. These factors were intake rate, leaching, sorption and screening.

Van der Ploeg and Beese (1977) showed that the soil moisture sampler distorts the existing gradient patterns in the soil in such a way, that around the ceramic cup exaggerated percolation rates are created. They state that the composition of the collected sample is not representative for one particular depth, but reflects some average composition of the surroundings. Van der Ploeg and Beese found that extraction rates with even a small vacuum applied, were much higher than the percolation rate under freely vertically draining conditions. They could find no relation between the amount of soil water extracted and the freely percolating soil water.

It thus appears that a great deal of care must be taken in extrapolating results obtained with the use of soil water samplers to conditions which actually exist in

the unsaturated zone. This is especially true when dealing with environments where solute concentrations are low. Little has been written on the effect of the ceramic cups on low organic concentrations which may be present in the soil water, and this is an area which needs more research.

The soil moisture sampler most commonly used in monitoring the unsaturated zone is a pressure vacuum model which was developed by Parizek and Lane (1970). This sampler can be effectively used up to depths of 50 feet, and can be used to collect samples over a long period of time. This particular model has the advantage that it can be installed in a given location, and the samples removed from the sampler at another location. For example, the sampler can be installed under an active landfill and the samples collected at the side of the landfill.

The Extraction Procedure (E.P.) Toxicity test was proposed in December, 1978, as one of the criteria to be used in determining whether a waste should be classified as hazardous or not. Since that time many industries have challenged the validity of the test, especially in terms of its reproducibility, and have reported that the reproduceability of the test varied with the type of waste, the elements analyzed for, and the analytical technique used (Rose et al. 1981).

In addition, since EPA has listed National Drinking Water Standards for only eight heavy metals and six pesticides, it is possible for a waste to pass the EP Toxicity test, and still contain harmful compounds. An example of this is textile industry wastes, which contain toxic dyes and chlorinated benzenes, but would pass the E.P. Toxicity test because these compounds are not measured (Anon 1980).

The E.P. Toxicity procedure was developed by the EPA as an attempt to measure the leaching potential of various wastes. In developing the procedure, the assumption was made that toxic wastes were being co-disposed of with actively decomposing municipal waste. This led to the adoption of .5N acetic acid as the leaching medium, since municipal landfills produce aggressive, acidic wastes (McKown et al. 1981). One of the criticisms of the test, especially as it applies to landfarming of oily residues, is that the leaching conditions are too harsh (Dallaire 1981). However, recent studies indicate that rainfall with pH of 5 or less falls regularly over large areas of the U.S., especially the Eastern U.S. as far south as Florida (Ember 1981, Cowling 1982). Thus, in some instances, the leaching medium may not be aggressive enough. The E.P. Toxicity procedure does not yield accurrate results when used with wastes containing free oil.

CHAPTER 3

SITE SELECTION

At the start of this project, the intention was to select four sites across the country which had been used for the land treatment of oily residues from petroleum refining. The idea was to select sites in varying climates, so that closed sites under differing conditions could be evaluated. However, sites outside of Oklahoma could not be obtained, despite the assistance of the American Petroleum Institute.

In selecting sites for use in this study, several factors in addition to climate were considered. These factors were

(1) The availability of data on what had been applied to the site.

(2) The time period for which the site had been used.

(3) The time period for which the site had been inactive.

(4) The management practices at the site.

(5) The depth to groundwater

(6) The presence of monitoring wells.

Several refineries in Oklahoma which operated land treatment sites were visited, and based on these visits and discussions with plant personnel, three sites were selected for use in the project. In all three cases, a section of what had previously been active land treatment sites was selected for use.

In evaluating the sites one significant problem was encountered. Although land treatment of oily residues has been used for many years at oil refineries, records of operational procedures have only been maintained at most refineries since the late 1970's. As a result of this, limited application and management data was available for all of the sites evaluated in Oklahoma. A synopsis of the data available for the three sites selected is presented below.

Site 1

This site had been used for land treatment since July 1976. It was used in 1976, 1977 and 1979, but no analytical work was performed. The plot was not used in 1978. Starting in February 1980, records were kept of the type and quantity of waste being applied to the site. A tank farm was originally located at this site, but no data is available on spills etc., which might have occurred during the time the tank farm was located here.

The last application of residues to the section of the site investigated was on January 5, 1981. Available

data shows that in 1980, approximately 170 cubic meters (1091 barrels) of oil were applied, with an oil content ranging from 3.3 to 79.2 percent. In 1981, 7 cubic meters (42 barrels) were applied with an approximate oil content of 2%. The 1980 figures suggest an annual loading rate of about 3% w/w of oil to soil. The research was carried out on an area of approximately 0.3 hectares (.75 acres).

Site 2

This site has been used as a land treatment site since March 1974. It was used until the middle of 1976, with oil sludge and biosludge being applied in amounts of 157 to 236 cubic meters (400 to 600 barrels) of oil/-hectare (2.47 acres). Precise analytical data is not available, but laboratory records indicate a 38% oil content for the oily sludge, and a 12% oil content for the biosludge. The research was carried out on an area approximately 0.2 hectares (0.5 acres) in size.

Site 3

Site 3 has been in operation as a land treatment site since 1975. Prior to this, the oily residues were dumped in large pits which had a total capacity of 72,620 cubic meters (456,814 barrels). These pits were emptied in 1975, and their contents applied to the land treatment site. The area of the site is 2.85 hectares (7.04 acres), and personnel at the refinery estimated a water

content of 60% for the contents of the pits. This means that approximately 10,196 cubic meters (25,955 barrels) of oily residue per hectare were applied to the site at the start of the land treatment operation in 1975. Records available for the period 11/25/80 to 1/9/81 indicate a total of approximately 970 cubic meters (6,100 barrels) of oily residues were applied to the site over a six week period. The research was carried out on an area of approximately 0.12 hectares (0.3 acres).

No information was available, from any of the refineries, on the exact source and/or nature of most of the residues which had been applied to the sites. In the few cases where the source of the applied residues was recorded, the location on the site where the residues had been placed was not noted.

Figures 3.1, 3.2 and 3.3 are pictures of sites 2, 1 and 3 respectively. At site 2 the residues were applied to alternate strips of land 61 meters long by 4 meters wide (200' x 13'), while at site 1 and 2 the residues were appled to the whole site.

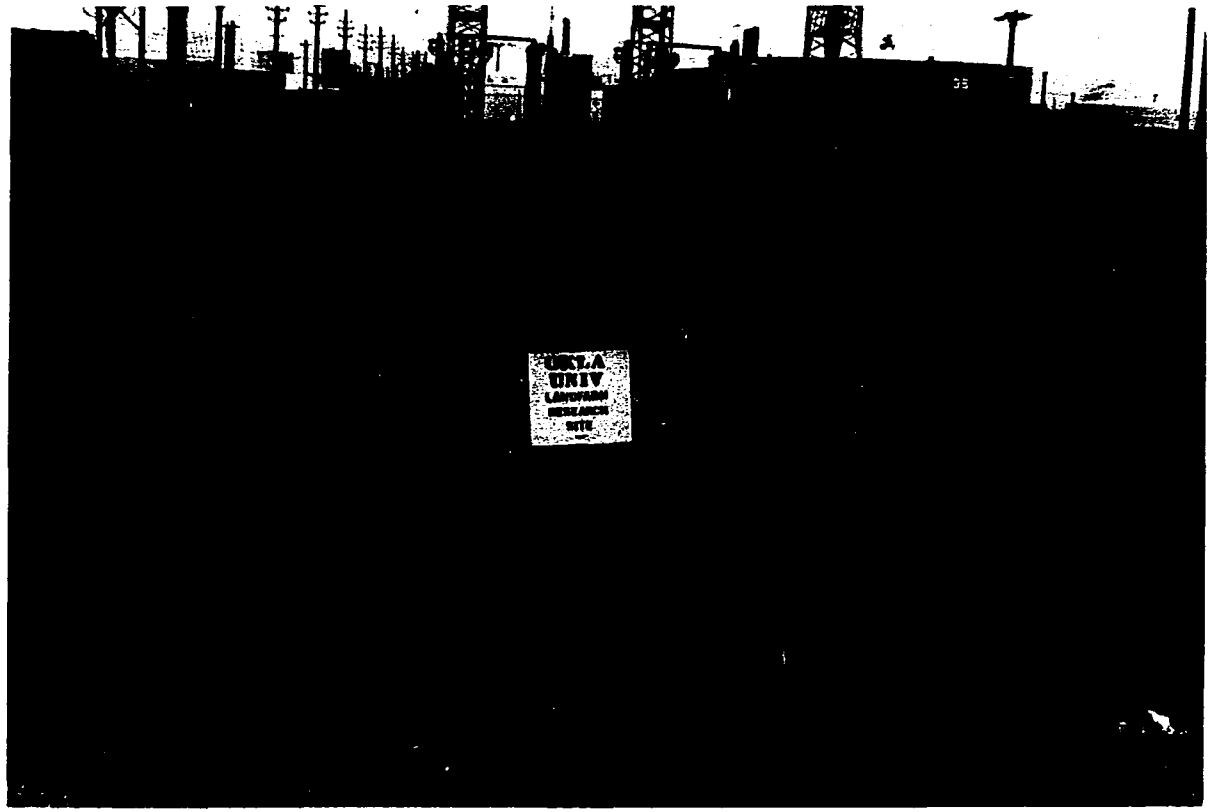

Figure 3.1 Site 2 showing the tilled and untilled strips. Poles in right foreground indicate the location of soil moisture samplers in area 6.

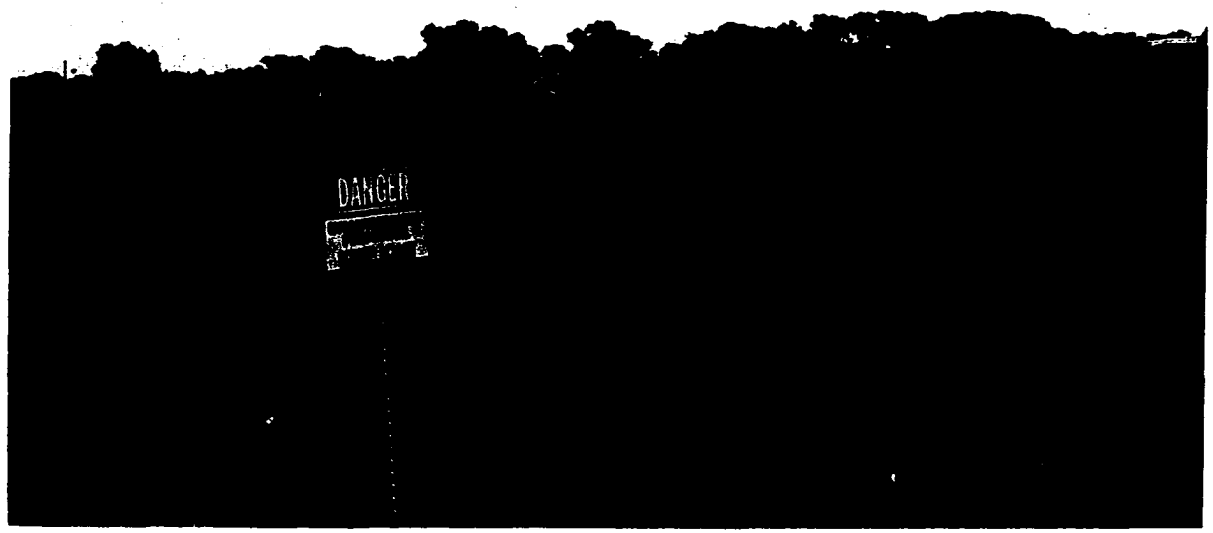

Figure 3.2 Site 1 prior to start of work at the site.

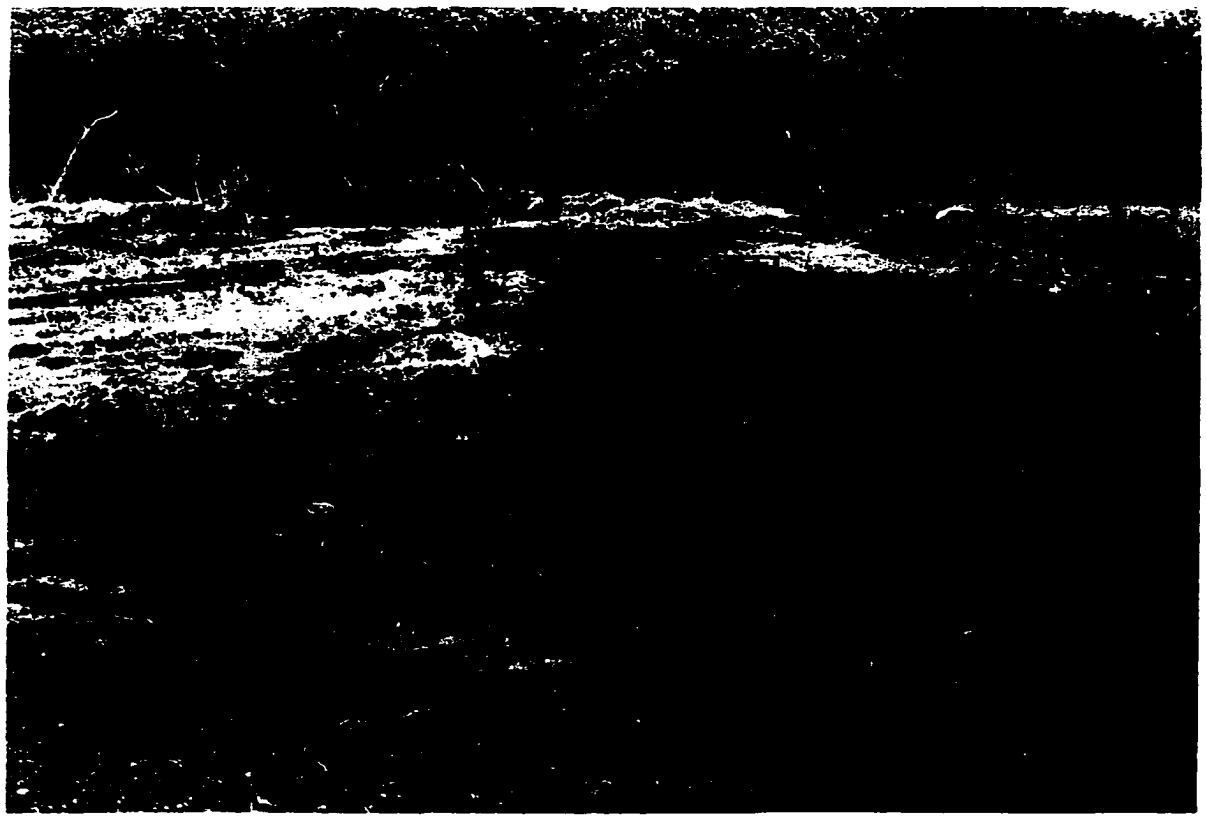

Figure 3.3 Site 3 showing the tilled and untilled section.

SAMPLING PROCEDURES

Each site was divided into six sections, after initial sampling and oil content analysis at sites 1 and 2. These initial samples were collected randomly. However, an examination of the results of this initial round of sampling revealed that there was considerable variability in oil content across the site. Thus, to obtain more representative samples, it was decided to subdivide the sites, and then sample randomly within each area, compositing the samples. Five cores were composited from each section, giving a total of 30 samples/site. This number of samples was enough to yield an error in the estimate of the means of a maximum of 1%, and usually less than 0.5% for the oil content of the site soil.

A visual inspection of the cores taken, coupled with the results of the initial oil content determinations, led to the decision to sample the top 25 cm. and the 25 centimeters directly below it, to ascertain the extent to which the oil had migrated. The samples were collected using soil sampling tubes. Initially Hankinson soil sampling tubes were used, but these proved too fragile for the types of soil being sampled, and stronger samplers were fabricated in the School of Civil Engineering and Environmental Science. The soil samples were all collected using these samplers, unless otherwise indicated.

Deep Core Sampling

The deep core samples were obtained by drilling a hole below the zone of incorporation using an auger, cleaning out the hole, and then using a soil core sampler to collect samples from the desired depth. In this way, samples up to a depth of 152 centimeters (60 inches) were collected at each site. Deep core samples were collected at each site each of the two years of the project.

Soil Pore Water Sampling

The soil water passing through the unsaturated zone beneath the zone of incorporation was also sampled. Sampling of the soil pore water was accomplished by installing soil moisture samplers (lysimeters) at a depth of approximately 1.2 meters (4 feet) at the sites. The sampler used was Model 1920, sold by Soil Moisture Incorporated of California. Before the samplers were installed, an evaluation was made of the methods suggested by the vendor for installation of the samplers. Field work was carried out to determine the most suitable method for installing the samplers. The following method of installing the samplers was adopted as a result of this evaluation.

A 10 cm. (4 inch) hole was drilled to the required depth, and thoroughly cleaned out, making sure that none of the oil contaminated soil from the zone of incorporation was in the hole. The bottom of the hole was tamped,

and then the sampler was seated in very fine-300 mesh-silica sand, so that the ceramic cup of the sampler was completely covered. Parent soil (15 cm.) was then put into the hole, and tightly tamped. A layer of dry bentonite clay was then put into the hole followed by more parent soil. The hole was filled to about 20 centimeters (8 inches) from the top with parent soil, which was added in small amounts and tightly tamped. Another layer of dry bentonite clay was then added (5-8 cm.) and the hole filled with soil. Figure 3.4 is a diagram of the mode of installation.

The samples collected were all identified by a code which identified the site from which the sample was taken, the date of collection and the type of sample. The sample could also be identified as being from a tilled or untilled area, in the case of site 2.

The site code consisted of a seven digit number with 1 or 2 letters after it, e.g. 1111282S or 1111281SW. The first digit identified the site, the next six the date, and the last two letters identified the sample type. The code 1111281S would refer to a soil sample from site 1 collected 11/12/81. The areas within the site were identified using the numbers 1 to 6, and the letter T or B to represent the depth 0-25 cm. and 25-51 cm. respectively. An additional T or U was used to differentiate tilled areas from untilled areas at site 2.

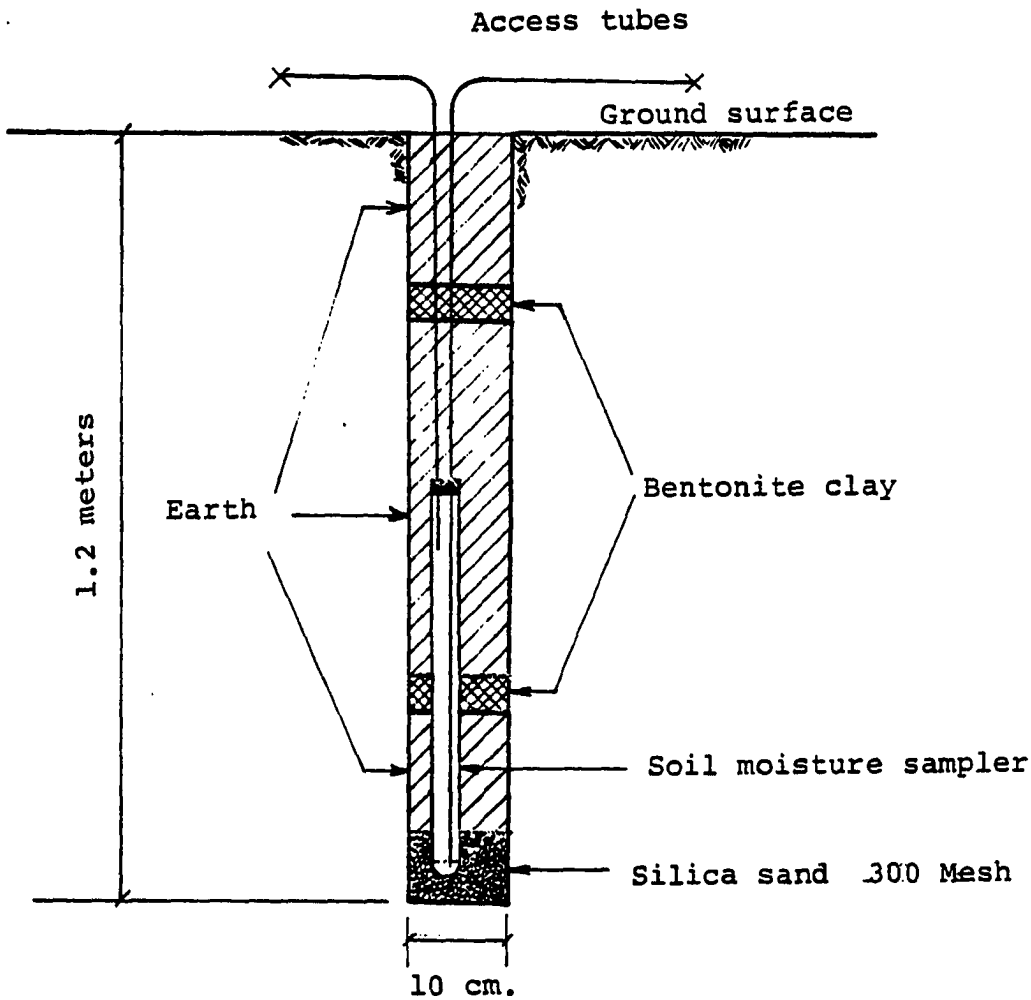

Figure 3.4 Method of Installation of Soil Pore Water Sampler

Thus:

1T - Top (0-25 cm.) sample from area 1

3TT - Top sample from the tilled section of area 3

2TU - Top sample from the untilled section of area 2

S - Soil sample

SW - Soil water sample.

The soil samples which were taken for purposes of comparison with the soil pore water samples, were taken at a distance of 6 feet from the soil moisture sampler.

CHAPTER 4

ANALYTICAL METHODS

Oil Content

Two procedures were used for oil content determinations. The oil content of the sludges and soil sludge mixtures was determined by extraction with dichloromethane, using the procedure of McGill and Rowell (1980). In this procedure, 10 grams of the sample were extracted for 4 hours using a Soxhlet extraction apparatus. Prior to extraction, the soil was ground so that it could pass through a 40 mesh sieve, and then quartered to obtain the desired sample size. The extract was then evaporated down to a volume of 15 to 20 ml on a steam bath, transferred to a preweighed aluminum dish, and allowed to air dry in a fume hood overnight. The sample was then purged with nitrogen gas, by directing a steam of the gas onto the surface of the residue in the aluminum dish. The purging was necessary to drive off any remaining dichloromethane. The residue and aluminum dish were then weighed, and the weight of oil determined. The thimbles plus soil were oven dried at 103°C, and the weight of dry soil obtained. The oil content was then expressed as a

per cent dry weight.

The oil content of the aqueous samples was determined gravimetrically, using method 413.1 from test "Methods for Chemical Analysis of Water and Wastes" published by the Environmental Protection Agency (March 1979).

Fractionation Analysis of Oil

Fractionation analysis on the oil extracts from the site soils was carried out using ASTM Method D-2007-73. Initial analyses were performed on standard oils obtained from the Agronomy Department at Texas A & M University, to verify the method.

Metal Analysis

Heavy metal analyses were carried out on sludges, site soil, soil pore water and the Extraction Procedure (E.P.) Toxicity extract. The sludges and site soil samples were analyzed using a digestion procedure obtained from the Environmental Protection Agency's Robert S. Kerr Environmental Research Laboratory (RSKERL) in Ada, Oklahoma. In this procedure, between 0.2 and 1 gram of sample was accurately weighed in an acid-washed beaker, 10 mls of concentrated nitric acid added to the beaker, and the mixture just evaporated to dryness. 10 more mls of acid were then added to the beaker, and the beaker was covered and allowed to reflux gently for a minimum of 2 hours. When ashing of the sample was complete, indicated

by the absence of vigorous reaction, the beaker was cooled, 1 ml of 30% H_2O_2 added and the digestion was continued. Additional 1 ml portions of H_2O_2 were added up to a maximum of 10 mls, until ashing was complete. This stage was denoted by no further changes in the color of the sample. The cover was then removed from the beaker, and the sample evaporated until just dry. Three mls of nitric acid were then added, the beaker heated to solubilize the residue, and then 25 mls of water were added. The beaker was then covered, and the contents allowed to digest for 1 hour. The sample was then transferred to a 100 ml volumetric flask, diluted to volume, and analyzed by Atomic Absorption Spectrophotometry.

The aqueous samples were prepared for analysis using methods 3010 or 3020 from "Test Methods for Evaluating Solid Waste-Physical/Chemical Methods" published by the Environmental Protection Agency.

All samples were analyzed on a IL Model 551 Atomic Absorption Spectrophotometer, equipped with a Model 655 furnace.

Chloride Analysis

The method used for chloride analysis of soils was taken from "Methods of Soil Analysis" published by the American Agronomy Society (Black et al., 1965). Both 1:5 and 1:1 ratios of soil to water were used. The chloride ion concentration in the soil pore water samples was de-

termined using method 325.3 - titritmetric determination with mercuric nitrate - taken from the EPA manual "Methods for Chemical Analysis of Water and Wastes".

pH Determination

The pH determination for soils was done according to the procedure outlined in Methods of Soil Analysis (Black et al., 1965).

The soil sample was diluted 1:1 with water and mixed for 30 minutes. The mixture was allowed to stand for one hour to settle, and then the pH was determined using an Orion Model 401 pH meter with an Orion Model 91-02 electrode.

Nitrate

Soil nitrate determinations were carried out using the phenoldisulfonic acid method described in part 2 of "Methods of Soil Analysis" published by the American Agronomy Society (Black et al., 1965). This procedure involves the development of a yellow color with phenoldisulfonic acid by the nitrate ion in an aqueous extract of the soil.

Available Phosphorus - Bray's Method

The method used determined the phosphorus in the soil soluble in NH_4F/HCl solution. The procedure used was taken from "Methods of Soil Analysis", edited by Black et al.

Total Organic Carbon

The total organic carbon content of aqueous samples was determined using a Beckmann Model 915 Total Organic Carbon Analyzer with an infra red detector. The total organic carbon content of the soil samples was determined in two ways. The first set of determinations were carried out using the Walkley-Black Method with external heat as described in "Methods of Soil Analysis" edited by Black et al. In this method, the carbon is oxidized with potassium dichromate at a temperature of 150°C. Later determinations were performed on a Leco Total Organic Carbon Analyzer.

Extraction Procedure (E.P.) Toxicity Test

The procedure followed was the one described in the May 19, 1980 Federal Register. Samples of 100 grams were used, with no filtration prior to extraction since the sample was relatively dry soil. The extraction was performed using an extractor built in the School of Civil Engineering and Environmental Science at the University of Oklahoma, to the specifications described in the May 19, 1980 Federal Register. Figure 4.1 shows the extractor. Filtration was carried out using a pressure filter with .45 micron pore openings.

The extract was analyzed for both metals and priority pollutants. The extract was prepared for these analyses using the procedures described in the sections on

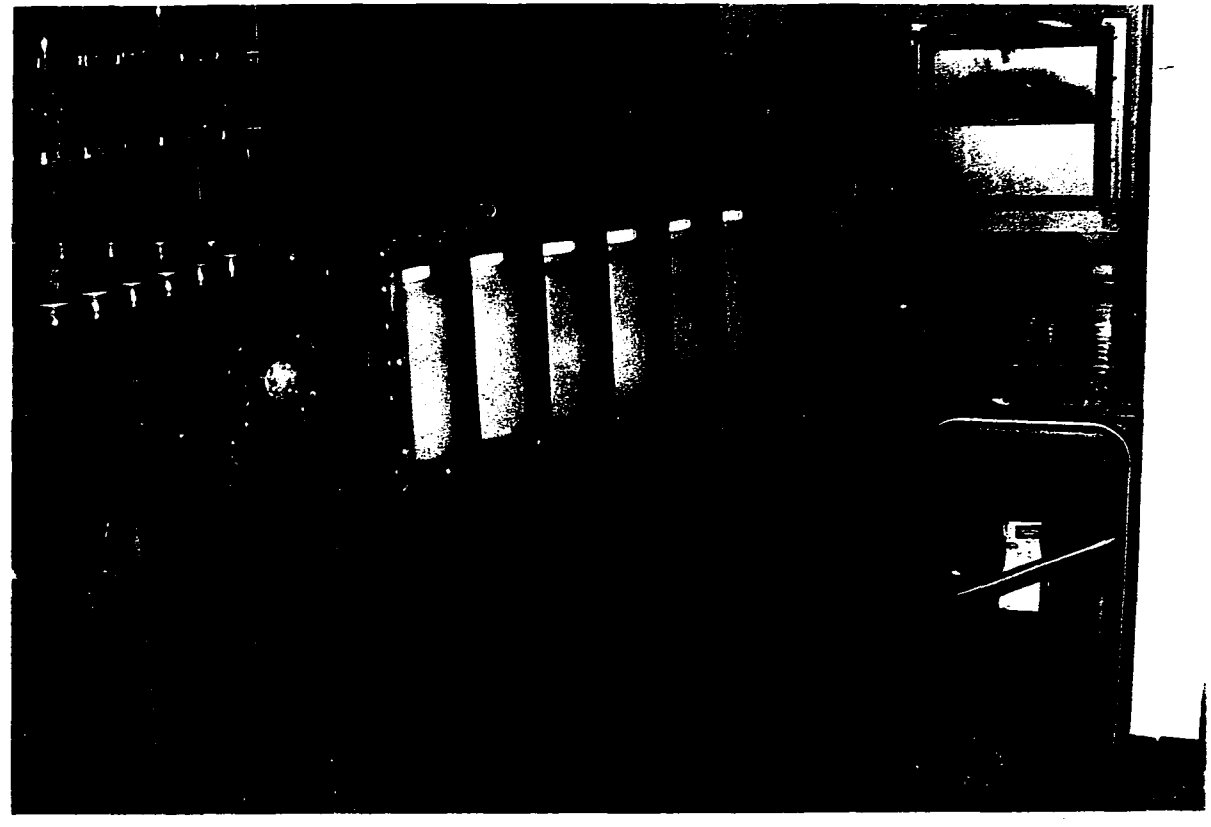

Figure 4.1 Extractor used in E.P. Toxicity test.

Metals Analysis and Priority Pollutant Analysis.

Priority Pollutant Analysis

The soil samples were extracted for priority pollutant analysis by using a combination of Methods 3540 and 3530 in the EPA Manual, "Test Methods for Evaluating Solid Waste". In the first part of the procedure, the solid sample was subjected to Soxhlet extraction using dichloromethane, as described in Method 3540. The extract from this procedure was concentrated to about 2.5 mls, and 0.5 mls removed for analysis for volatiles. The remainder was then extracted by Method 3530, yielding base/neutral and phenolics fractions.

The three fractions obtained in the extraction stage were then analyzed by a GC/MS system. The system used was a Hewlett-Packard 5985A Mass Spectrometer, with a HP 5740 Gas Chromatograph and associated data system. Two different columns were used to analyze the three fractions. The Base-Neutrals and Phenolics were analyzed on a DB-5, 30 meter, fused silica capillary column, and the volatiles were determined on a Carbopack C (60-80 mesh) coated with 0.2% carbowax 1500. The conditions under which the various fractions were run are given in Table 4.1.

Standards were run at the start of each day's analysis, and identified from the mass spectrum of each peak obtained in the chromatogram. The unknown samples

Table 4.1 GC Conditions for Priority Pollutant Analysis

	Volatiles	Base-Neutrals	Phenolics
Initial Temp.	60°C	50°C	60°C
Initial hold time	3 min.	1 min.	1 min.
Ramp rate 1 (time in min.)	8°/min.	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
Run Time	25 min.	40 min.	20 min.

Carrier gas - Helium

Flow rate - 14 ml/min. for capillary column
25 ml/min. packed column

were run and the resulting data stored on disk. Once all the samples were run, a standard file library of all the standards was created using a computer program written for identification and quantification called the IQ program. Each fraction - volatiles, base-neutrals and phenolics - had its own file. A data file was then set up for the sample fractions, and matched against the files for the standards. The resulting printout was then analyzed for matches between the standards and unknown samples, and the concentrations of the compounds identified in the samples were calculated using response factors for the standards.

Cation Exchange Capacity

The cation exchange capacity of the soil at each site was determined using the ammonium saturation method. This procedure was taken from "Methods of Soil Analysis" edited by Black et al. The procedure entailed saturation of the air-dried soil with neutral 1N Ammonium acetate, followed by removal of the absorbed NH_4^+ by passing air through a suspension of the NH_4^+ saturated soil in Na_2CO_3 solution. The displaced NH_3 was then passed into a container with H_2SO_4. By determining how much acid reacted with the NH_3, the concentration of NH_4^+ ion could be determined, and hence the cation exchange capacity of the soil.

QUALITY ASSURANCE/QUALITY CONTROL

A QA/QC program was implemented at the beginning of the project. This program had two main parts. Part 1 involved sample collection, transportation and storage, and Part 2 involved the determination of blanks, replicates and spikes.

Each sample collected was assigned an identifying code, which contained information on the site, date and type of sample collected. Samples were placed in a cooler immediately upon collection, to keep them cool until they could be transported to the laboratory and refrigerated. The samples were stored in a refrigerator dedicated to project samples, at 4°C, until they were analyzed. Soil samples were collected in Ziploc plastic bags and aqueous samples in borosilicate glass bottles with teflon-faced screw caps. A log book of all site visits and samples collected was maintained. Aqueous samples to be analyzed for metals were adjusted to pH <2 with nitric acid as soon as they arrived at the laboratory. pH and C.O.D. analyses were performed on the samples within 24 hours of collection. All samples for priority pollutant analysis were extracted within one week of collection, and analyzed within one month of extraction.

Glassware used for priority pollutant analysis was solvent washed, detergent washed, rinsed with tap water,

distilled water and oven-dried. The K-D flasks and concentrators were also cleaned with chromic acid prior to each set of extractions. After each batch of samples from one site was run, the glassware was heated to 400°C in a furnace after the cleaning sequence described above.

Glassware for metal analyses was washed with detergent, and then acid-rinsed with nitric and hydrochloric acids. After a final rinse with distilled water, the glassware was oven-dried. Glassware used for other analyses were cleaned using standard laboratory cleaning procedures.

The quality control procedures used in the determination of priority pollutants centered mainly on the determination of blanks and the use of duplicate determinations. Pesticide grade solvents were used in all extractions. Spikes were also determined on the aqueous samples. No studies were done on recoveries from the different soil matrices, because of time and money restrictions.

The GC/MS system was tuned on a daily basis with perfluorotributylamine (PFTBA). Decafluorotriphenylphosphine (DFTPP) Standards were run to check the relative ion abundance. The mass spectrometer source was heated to a temperature of 274°C periodically to remove contaminants.

Duplicates, spikes and blanks were also run on the

samples analyzed for metals. The QC data is given in Appendix A.

Procedural blanks were run with every set of Extraction Procedure Toxicity determinations. Ultrex nitric acid from J.T. Baker Chemical Co., was used in the digestion of the extract for metal analysis. These blanks served as controls for the level of metal contamination introduced by the extraction and filtration steps, as well as the digestion step.

In all cases, the concentrations of the blanks were subtracted before the final metal concentrations were calculated. Table A-1 lists blanks for soil pore water, E.P. Toxicity and soil core samples. A large number of blanks were not run for soil samples, because large numbers of the samples were digested simultaneously. One blank was run per set of digestions for soil and soil pore water samples. Table A-2 lists duplicate determinations on soil samples analyzed for metals.

As a part of the QC for the determination of organics, blank determinations were run on several samples of soil, soil pore water and E.P. Toxicity extracts. Chloroform was an omnipresent contaminant, and showed up in all samples analyzed for volatiles. Trichloroethene showed up in two blanks, toluene in one and benzene in another. One other sample indicated the presence of phenolics, but this was traced to contamination of the

vial used to store the sample.

A total of 10 blanks were taken through the whole extraction and analysis procedure, and the only compounds identified were those mentioned above. The QC data for organics is presented in Tables A-3 to A-5.

Quality control procedures for oil content analysis were also implemented. At the start of the project, a brief study on the recovery of oil from soil was carried out. Recoveries ranged from 94% to 98%. Duplicates were run during the project, and Table A-6 presents the duplicate data. The mean of the duplicates was used as the experimental value.

Quality control for the other tests was as follows:

(1) pH - Standardization of the meter before use and the determination of duplicates on soil samples. For aqueous samples only one determination per sample was possible

(2) Nitrate and Phosphate - A standard was run with each set of samples to check the calibration curve, and one duplicate determination was carried out for each set of samples.

(3) T.O.C. and C.O.D. - QC was by means of blanks and duplicates.

(4) Cation exchange capacity - One blank was carried through the procedure for each set of the samples run. Duplicates were also run.

CHAPTER 5

EVALUATION OF SITE CHARACTERISTICS

PRIORITY POLLUTANTS

The site soil was tested for the presence of selected priority pollutants. The samples were first extracted with methylene chloride using the Soxhlet extraction procedure, and then that extract was subjected to separatory funnel liquid - liquid extraction. These procedures are Methods 3540 and 3510 in "Test Methods for Evaluation of Solid Waste (2nd edition)".

Three different sets of samples from each site were analyzed during the project, to identify any persistent organics present as definitely as possible. Table 5.1 lists the organic compounds evaluated, and Table 5.2 the compounds identified as present at the sites. This identification is essentially qualitative, since no studies on the recovery of organics from soil matrices were carried out during this project. However, Tables B-1 to B-3 in Appendix B contain the concentrations of the compounds identified at the sites. These values are intended as a guide to the order of magnitude of the concentrations of the compounds identified at the sites.

Table 5.1 Priority Pollutants

Base/Neutrals

1,3-Dichlorobenzene
1,4-Dichlorobenzene
Hexachloroethane
1,2-Dichlorobenzene
Hexachlorobutadiene
Naphthalene
Bis(2-chloroethyl) ether
Nitrobenzene
Bis(2-chloroethoxy) methane
Hexachlorocyclopentadiene
2-Chloronaphthalene
Acenaphthylene
Acenaphthene
Isophorone
Fluorene
2,6-Dinitrotoluene
1,2-Diphenylhydrazine
2,4-Dinitrotoluene
Hexachlorobenzene
4-Bromophenyl phenyl ether
Phenanthrene
Anthracene
Dimethylphthalate
Diethylphthalate
Fluoranthene
Pyrene
Di-N-butylphthalate
Butylbenzylphthalate
Benzidene
Chrysene
Bis(2-ethylhexyl) phthalate
Benzo(a) anthracene
Benzo(b) anthracene
Benzo(a) pyrene
Dibenzo(a,h) anthracene
Indeno(1,2,3-c,d) pyrene
Benzo(g,h,i) perylene
Lindane
Methoxychlor
Endrin
2,4-D
2,4,5-TP
Benzo(k) fluoranthene

Phenolics

2-Chlorophenol
Phenol
2,4-Dichlorophenol
2-Nitrophenol
p-chloro-m-cresol
2,4,6-Trichlorophenol
2,4-Dimethylphenol
2,4-Dinitrophenol
4,6-Dinitro-o-cresol
4-Nitrophenol
Pentachlorophenol

Volatiles

1,4-Dichlorobutane
2-Bromo-1-chloropropane
1,1-Dichloroethane
Trans-1,2-dichloroethene
Chloroform
1,2-Dichloroethane
1,1,1-Trichloroethane
Carbon tetrachloride
Bromodichloromethane
1,2-Dichloropropane
Trichloroethene
Dibromochloromethane
1,1,2-Trichloroethane
Benzene
Bromoform
1,1,2,2-Tetrachloroethene
1,1,2,2-Tetrachloroethane
Toluene
Chlorobenzene
Ethylbenzene

Table 5.2 Priority Pollutants Identified in Soil at Land Treatment Sites

	Site 1	Site 2	Site 3
Anthracene	x	x	
Phenanthrene	x	x	
Fluoranthene	x		x
Pyrene	x	x	x
Naphthalene	x	x	
Chrysene	x		
Benzo(b)fluoranthene	x		
Benzo(a)anthracene	x		x
Benzo(a)pyrene	x		x
Dibenzo (a,h)anthracene	x		x
Benzo(g,h,i)perylene	x		
Isophorone	x	x	x
Bis(2-ethylhexyl)phthalate	x	x	x
Butylbenzylphthalate	x	x	
1,2-diphenylhydrazine		x	
Phenol	x	x	x
Pentachlorophenol	x	x	
4-Nitrophenol		x	
2-Nitrophenol		x	
2,6-dinitrotoluene			x
Benzene	x	x	x
Toluene	x		x
Ethylbenzene	x		x
Bromoform			x

x Denotes compound which was present.

At site 1, most of the 19 compounds identified were at very low concentrations (<.001 ppm). However, some compounds (polynuclear aromatics) were present at quite high concentrations. These compounds were also the ones present in the highest concentrations at site 3. Phenol showed a definite trend at site 1, increasing in concentration over the sampling period 11/10/81 to 12/1/82. Thirteen of the 19 compounds were polynuclear aromatics (PNA's).

At site 2, 13 compounds were identified at the site, 6 were PNA's and 4 were phenolics. The compounds present at highest concentrations were again polynuclear aromatics. Trace amounts of phthalates were found, but no volatiles.

Thirteen compounds were identified at site 3, with 6 of them being PNA's. Four volatiles were also identified at this site.

Only pyrene, isophorone, bis(2-ethylhexyl)phthalate, phenol and benzene were identified at all three sites. Volatile compounds were identified mainly at sites 1 and 3, which had residues applied more recently than site 2.

Table B-4 in Appendix B lists compounds which were found in the background samples taken at the three sites. The concentrations of the compounds identified in the background samples were quite low, but so were the concentrations of most compounds identified at the sites.

The reason for the presence of these compounds in the background samples is not clear. All of the sites were located at refineries, and the background samples were taken near the land treatment area itself. It may be that the background samples were taken too near to the treatment area, and the soil was slightly contaminated, or these compounds may be present naturally, or transported by air from other locations. Phthalates, for example, are ubiquitous in the environment, and bis-(2-ethylhexyl)phthalate was present in the background samples from all sites. Other compounds present in the background samples from all sites were chrysene and benzo(a)anthracene.

OIL CONTENT

Determinations were made of the oil content of the soil at each of the 3 sites during the course of the project. The objective of these tests was to determine:

(1) The variability in the oil concentration across the site.

(2) Whether oil was still present at the site.

(3) The extent to which the oil was degraded over the research period.

(4) The extent to which the oil had migrated vertically.

A part of each site was tilled during the project to

see if tilling had any effect on the rate of degradation when compared to the untilled area.

Variability of Oil Concentration

As described in the section on sampling, the research area at each site was divided in 6 sections, and composite samples taken from each section. These composites were made up of 5 individual cores, and were thoroughly mixed before analysis. It is apparent from the oil concentrations present in the different sections at each site, that there was great variation in the oil content across the site as a whole. However, there was also great variation within each section at the sites. Table 5.3 shows oil content values obtained from individual cores taken at site 3. These cores were from three diffenent areas at site 3, and show the variablity of oil concentration across the site. Table 5.4 shows the results obtained at site 2 when individual cores were analyzed from one area and compared to a composite sample taken from the same area. It can be seen that at site 2, the oil concentration of the composite of 5 cores was very close to the mean of the concentrations of 5 individual cores taken from the same location.

Oil Content of Site Soil

The soil at each site was sampled periodically over the project period, and the samples analyzed for oil content. A part of each site was tilled, so that the rate

Table 5.3 Variability of Oil Concentration at Site 3

Area 1	Sample #	% Oil
	1	5.0
	2	8.7
	3	3.6
	4	4.1
	5	2.9
	6	7.7
	7	3.6
	8	3.8
	9	2.3
	10	5.3
	Mean concentration =	4.7
	Standard deviation =	2.07
	Variance =	4.28

Area 2	Sample #	% Oil
	1	4.1
	2	5.0
	3	4.5
	4	6.2
	5	8.8
	Mean concentration =	5.7
	Standard deviation =	1.88
	Variance =	3.55

(continued)

Table 5.3 (continued)

Area 3	Sample #	% Oil
	1	14.1
	2	8.3
	3	8.3
	4	4.7
	5	12.9
	6	7.2
	7	13.8
	8	5.7
	Mean concentration =	9.4
	Standard deviation =	3.71
	Variance =	13.74

Table 5.4 Variability of Oil Concentration at Site 2

Area 6 Top	Sample #	% Oil
	1	1.5
	2	4.2
	3	6.3
	4	4.5
	5	6.5
	Composite	4.7
	Mean concentration =	4.6
	Standard deviation =	2.02
	Variance =	4.07

Area 6 Bottom	Sample #	% Oil
	1	0.9
	2	3.8
	3	0.3
	4	0.4
	Composite	1.7
	Mean concentration =	1.4
	Standard deviation =	1.65
	Variance =	2.74

of degradation in the tilled vs. the untilled sections could be evaluated. At site 1, half of the site was tilled, and the other half left untilled. At site 2, the land treatment site had had the residue applied to alternate strips of land. At this site, half of each strip was tilled, and the other half left untilled. At site 3, only a small portion of the site was tilled - Area 6.

Results

Table C-1 - Appendix C - shows the oil content concentration in the 0-25 cm (T) and 25-51 cm (B) layers of soil at the three sites. At site 1, areas 4, 5 and 6 were tilled. At site 3 only area 6 was tilled, while half of each area at site 2 was tilled.

Site 1

At site 1, there was a significant difference between the site oil content and the background for both the top (0-25 cm) and bottom (25-51 cm) levels ($\alpha = .05$). Table 5.5 presents the average oil concentrations at site 1. There was no significant difference in the oil concentration of the top and bottom layers over an 8 month period, which means that little or no degradation or migration had taken place over that period of time. The paired t-test at a 95% confidence level was used for the latter comparison.

Site 2

At site 2, as mentioned before, the strips with the

Table 5.5 Oil Content Data - Means Site 1

Date	Mean %	Std. dev.	Variance
*Background Top	0.56	0.30	0.090
*Background Bottom	0.13	0.06	0.003
4/8/82			
Top	4.90	1.52	2.30
Bottom	0.64	0.35	0.12
12/1/82			
Top	5.62	2.33	5.45
Bottom	1.85	1.40	1.96

* Mean of all background concentrations.

Table 5.6 Oil Content Data - Means Site 2

Date	Mean %	Std. dev.	Variance
*Background Top	0.43	.152	.023
*Background Bottom	0.40	0.10	.010
4/6/82			
Top, tilled	2.63	0.96	0.92
Bottom, tilled	0.78	0.37	.14
Top, untilled	2.95	0.52	0.28
Bottom, untilled	-	-	-
7/8/82			
Top, tilled	2.58	0.95	0.902
Bottom, tilled	1.08	.33	0.11
Top, untilled	2.60	1.72	2.97
Bottom, untilled	1.17	0.58	0.34
11/19/82			
Top, tilled	2.93	1.46	2.14
Bottom, tilled	1.46	1.31	1.72
Top, untilled	2.65	1.67	2.79
Bottom, untilled	1.08	1.14	1.29
2/16/83			
Top, tilled	2.97	1.70	2.89

* Mean of all background concentrations

oil applied had one half of each strip tilled 4 times during the research project. The oil content of the site soil did not change significantly over time. There was no significant change between March 1982 and February 1983 in the concentration of oil in the top tilled section of the site. There was no significant change in the oil concentrations of the site soil over the period January to November 1982. There was also no significant difference between the oil content of the tilled and untilled sections of a given strip at the end of a 12 month period.

The site oil concentrations top (0-25 cm) and bottom (25-51 cm) were all significantly higher - 95% confidence level - than background, except for the bottom tilled sample of 4/6/82. The mean concentrations of oil at the site are given in Table 5.6. It should be noted that average oil content of the top samples at this site were quite low, ranging from 2.58% to 2.95%. The oil content of the background top sample of 8/5/82 was not included in the calculation of the mean background site concentration, but was treated as an outlier. This was done because the sample was apparently taken from an area which was contaminated with oil after research work was started at the site.

Site 3

The same trend as at the other two sites was noted

here. There was no significant change in average oil content of the site between March 1982 and June 1983. However, there was a significant difference between the oil concentration of the site soil and the background concentrations. A 95% confidence level was used for the statistical analysis of the data. The mean site oil concentration values are given in Table 5.7.

Discussion of Results

There was not significant degradation or migration of the oil present at the sites during the research period. A number of factors could account for this lack of degradation. These include:

(1) The levels of nitrogen in the soil were too low and inhibited microbial metabolism of the oil. No nutrients were added to the sites during the research period, and very low levels of nitrogen were found in the site soil. Table 5.8 shows levels of nitrogen and phosphorus found at the sites.

(2) There were long periods during which the site soil was quite wet, which could have inhibited the aerobic microorganisms by creating anaerobic conditions in the soil.

(3) The oil at the site contained appreciable amounts of polynuclear compounds, which are difficult to metabolize. Table 5.9 lists the

Table 5.7 Oil Content Data - Means
Site 3

Date		Mean %	Std. dev.	Variance
*Background Top		0.57	0.50	0.25
*Background Bottom		0.10	0.0	0.00
3/26/82				
	Top	8.7	2.90	8.42
	Bottom	2.7	4.57	20.85
6/7/83				
	Top	9.03	4.85	23.56
	Bottom	5.13	4.62	21.42

* Mean of all background concentrations.

Table 5.8 Nitrogen and Phosphorus in Soil at Site*

Location	ppm N in Soil	ppm P in Soil
Site 1		
Area 1	1.37	140
Area 2	1.90	182
Area 5	1.44	193
Area 6	1.47	245
Background	0.06	875
Site 2		
Area 1	4.6	171.5
Area 3	3.8	367.5
Area 4	5.4	490.0
Area 5	7.0	280.0
Area 6	12.7	350.0
Background	12.9	52.5
Site 3		
Area 3	<0.1	<0.1
Area 4	<0.1	<0.1
Area 5	<0.1	<0.1
Area 5	<0.1	<0.1
Area 6	<0.1	<0.1
Background	<0.1	0.8

* Top 25 cm of soil

Table 5.9 Composition of Oil at Sites 2 and 3

	Asphaltenes %	Saturates %	Polar Compds %	Aromatics %
Site 2				
6T	18.0	28.0	32.0	22.0
6B	8.4	27.4	30.5	33.7
Site 3				
5T	12.4	32.4	37.6	17.6
4B	8.2	35.8	34.9	21.1

fractions found in the residues from sites 2 and 3.

At site 2, where the effect of tilling on the rate of degradation was evaluated, there was no significant change in the oil content of the tilled and untilled sections over a 14 month period. It must be noted that degradation might have been inhibited by low nitrogen levels, but this site had not been in use for over six years, and oil was still present in some locations at concentrations above background.

Oil was present below the till zone (0-25 cm) and as deep as 45-50 cms at all 3 sites. This suggests strongly that vertical migration of oil below the till zone occurs; occasional deep tilling or discing of the soil may be necessary to bring this oil up to the aerobic upper soil layers where it can be degraded.

The raw oil content data is given in Appendix C.

METALS

The concentration of selected heavy metals in site soil was determined, and compared to background metal concentrations. A 95% confidence level was used in all statistical tests unless otherwise stated. Three different sets of samples were taken over a 12 month period and were analyzed at sites 1 and 2, and two sets of samples at site 3. The sites were sampled as described

in the section on oil content.

At site 1, Cu, Pb, Ag and Zn were present at levels significantly above background of the top 25 cm., in at least 2 sets of samples. Cr and Ni showed up as significant in one set of samples. The data is presented in Appendix C. No samples from the 25-51 cm zone showed significantly increased metals concentrations.

At site 2, samples collected in the first year showed some metals at levels significantly above background, but the sample collected in the second year showed no significant increase in metal concentration of either the top or bottom zones. Co, Ni and Al were present at elevated concentrations in all 3 sets of top samples while Cu, Co and Al were present at elevated concentrations in two sets of bottom samples.

At site 3 only chromium shows up at concentrations above background in both sets of top samples. Table 5.10 lists the metals found at concentrations significantly above background at the sites.

The absolute concentration of metals in the site soil must also be considered in evaluating the metals data. The variability of the data can lead to findings of no significant concentration above background, even though some of the values used in the test may be quite high.

At site 1, the samples of 6/14/82 had mean Zn, Cr,

Table 5.10 Metals Found at Concentrations Significantly Above Background

Site 1

Date	α =.05		α =.1	
	Top	Bottom	Top	Bottom
7/28/81	Cu Pb Zn Ag		Co	Al
11/10/81	Cu Pb Zn Cr Ag			Cr
6/14/82	Ni Pb		Cu	

Site 2

Date	α =.05		α =.1	
	Top	Bottom	Top	Bottom
7/21/81	Co Ni Al	Cu Co Al Cr Ag	Pb Zn Cr	Zn Ag
11/28/81	Cu Co Ni Pb As Al Cr Ag	Cu Co Pb Zn Al Ni		As Al Cr
6/16/82	Co Al Ni			

(continued)

Table 5.10 (continued)

Site 3

Date	α =.05		α =.1	
	Top	Bottom	Top	Bottom
11/17/81	Cr	Pb	As	Cu
		Zn	Cu	Ni
		Al	Pb	Cr
			Zn	Ag
6/29/82	Zn	Zn		
	Cr	Ni		

Cu, Pb and As concentrations of up to 387.0, 274.7, 253.5, 144.0 and 344.0 mg/kg, respectively, and yet of these 4 only the Pb concentrations was found to be significantly above background levels. Cd, Ni, Ag and Co were generally present at concentrations of <30 mg/kg, with Cd usually <1 mg/kg.

At site 2, all metals determined were present at low concentrations, including those found to be present at concentrations above background. As, Cu, Cd, Co, Ni and Ag were all generally at concentrations <30 mg/kg, while Zn, Cr and Pb were present at concentrations up to 143.3, 178.8 and 78.8 mg/kg, respectively, in the top layer of soil.

At site 3, concentrations were generally below 100 mg/kg, but the same trends noted at sites 1 and 2 were again present. Cr and Zn were present at levels significantly above background, but their concentrations were a maximum of 66.6 and 71.4 mg/kg, respectively. Table 5.11 presents the mean metal concentrations at the sites. The raw data is presented in Appendix C, Table C-2.

A number of trends may be noted with the metals data. The metals which show up in the highest concentrations at any of the sites are Zn, Cr, Pb, Cu, Ni and As. Table 5.12 lists accepted concentrations of metals in soil in ppm for the metals of interest. It can be seen that Zn, Ni and Cu at site 1 were the only metals whose

Table 5.11 Mean Metal Concentrations at Sites (mg/kg)

SITE CODE 1061482S

Metal	Mean		Standard Deviation		C.V. *	
	T	B	T	B	T	B
Ba	112.3	93.6	67.0	7.5	59.7	8.0
Cu	135.3	34.3	69.1	36.1	51.0	105.1
Cd	<1.0	<1.0	-	-	-	-
Ni	27.7	18.7	4.5	4.7	16.3	25.3
Pb	88.7	28.7	20.3	24.2	22.9	84.4
Zn	387.0	187.3	162.5	121.6	42.0	64.9
Cr	218.3	74.7	135.9	57.6	62.3	77.08
Ag	9.0	3.3	7.2	0.6	52.0	17.3
SITE CODE 1070281S						
Cu	253.5	96.0	43.4	67.8	17.1	70.6
Cd	<1.0	<1.0	-	-	-	-
Co	24.0	19.5	3.5	4.9	14.4	25.3
Ni	109.2	59.7	107.3	26.6	98.3	44.5
Pb	144.0	52.7	76.0	38.0	52.8	72.2
Zn	536.7	157.3	115.1	93.4	21.5	59.4
Cr	274.7	67.3	88.1	53.1	32.1	78.9
Ag	23.0	7.5	7.5	7.8	32.0	103.7

* C.V. coefficient of variation = std. dev/mean x 100

(continued)

Table 5.11 (continued)

SITE CODE 1111081S

Metal	Mean		Standard Deviation		C.V.	
	T	B	T	B	T	B
As	344.0	370.0	76.4	42.4	22.2	11.5
Cu	145.2	25.5	53.5	9.2	36.8	36.0
Cd	2.8	2.5	2.2	2.1	77.4	84.9
Co	9.6	8.5	4.3	2.1	45.2	25.0
Ni	80.8	25.0	84.6	2.8	104.7	11.3
Pb	102.0	38.0	30.7	7.1	30.1	18.6
Zn	334.6	59.5	125.2	19.1	37.4	32.1
Cr	153.4	55.0	70.2	2.8	45.7	5.1
Ag	14.6	3.5	3.9	2.1	26.8	60.6
SITE CODE 2061682S						
Ba	9.0	7.0	1.4	1.4	15.7	20.2
Cu	19.5	8.0	14.8	2.8	76.2	35.4
Cd	1.0	1.0	-	-	-	-
Ni	10.0	10.5	2.8	0.7	28.2	6.7
Pb	45.5	11.0	48.9	0.0	107.2	0.0
Zn	106.0	51.5	76.4	24.7	72.0	48.1
Cr	96.0	31.5	79.2	6.4	82.5	20.2
Ag	3.0	3.0	0.0	0.0	0.0	0.0

(continued)

Table 5.11 (continued)

SITE CODE 2072181S

Metal	Mean		Standard Deviation		C.V.	
	T	B	T	B	T	B
Cu	90.7	21.4	98.6	7.2	108.6	33.7
Cd	<1.0	<1.0	-	-	-	-
Co	24.6	26.2	3.0	4.2	12.2	16.0
Ni	53.7	62.8	15.9	25.9	29.5	41.2
Pb	78.8	47.7	66.3	43.1	84.1	90.5
Zn	136.3	61.2	135.8	53.6	99.6	87.6
Cr	178.8	119.5	158.9	57.9	88.9	48.4
Ag	5.5	5.0	3.0	1.4	54.8	28.2
SITE CODE 2111281S						
As	11.2	27.8	27.4	32.9	245.0	118.3
Cu	27.8	11.2	6.2	2.8	22.2	25.0
Cd	<1.0	<1.0	-	-	-	-
Co	6.2	9.0	4.4	1.5	71.4	17.2
Ni	29.2	38.2	18.1	44.2	61.9	115.8
Pb	75.2	24.0	26.6	7.8	35.3	32.4
Zn	143.3	51.5	28.4	18.1	19.8	35.2
Cr	121.7	15.0	53.2	17.5	43.7	116.5
Ag	3.8	2.0	1.2	1.4	30.5	70.7

(continued)

Table 5.11 (continued)

SITE CODE 3062982S

Metal	Mean		Standard Deviation		C.V.	
	T	B	T	B	T	B
Ba	71.5	123.5	34.5	67.0	48.3	54.2
Cu	10.8	24.8	3.8	14.8	35.1	59.7
Cd	<1.0	<1.0	-	-	-	-
Ni	22.3	13.8	4.2	4.8	18.8	34.8
Pb	19.5	54.8	7.6	42.8	38.9	78.1
Zn	71.5	123.5	34.5	67.0	48.3	54.2
Cr	46.3	54.8	17.1	15.5	37.0	28.4
Ag	<3.0	3.3	0.0	0.5	0.0	15.4
SITE CODE 3111781S						
As	86.8	113.2	76.9	136.5	88.7	120.6
Cu	38.2	29.0	20.4	18.5	53.3	63.8
Cd	<1.0	<1.0	-	-	-	-
Co	8.6	7.2	3.8	5.4	44.0	75.7
Ni	59.4	29.2	78.6	14.1	132.3	48.3
Pb	90.8	68.6	52.9	38.3	58.3	55.8
Zn	71.4	52.0	65.7	37.1	92.0	71.3
Cr	66.6	48.6	36.8	17.0	55.3	35.0
Ag	5.8	4.6	2.4	2.4	41.2	52.4

Table 5.12 Accepted Metal Concentrations in Soil as A Result of Irrigation or Other Activities

Element	Concentration (ppm)
As	500
Cd	20
Co	500
Cr	1,000
Cu	250
Ni	100
Pb	1,000
Zn	500

Brown (1980)

concentrations exceeded or even approached any of these limits. The list of metals in Table 5.12 is taken from a larger list of concentrations of metals acceptable for long-term and short-term (20 years) irrigation, developed by the National Academy of Science and the National Academy of Engineering in 1972, and cited by Brown and Associates (1980).

PH

The pH of the top (0-25 cm) and the bottom (25-51 cm) of site soil were determined during the project to see if the potential for solubilization of metals existed at the sites. The mean site concentrations are presented in Table 5.13. The pH values at all the sites were above the recommended 6.5 except for site 2 on 7/21/81, where the pH was 6.4. However later pH readings at this site yielded values of 7.2, which was well above the value of 6.5 recommended to minimize metal solubilization.

CHLORIDE

The chloride ion concentrations of the site soil was significantly higher than background at all three sites. Only 1 set of determinations were made, therefore, variation over time could not be observed. However, the chloride ion concentration of the soil pore water did decrease over time, and the same trend could be expected for soil chloride ion concentration. Table 5.14 shows the mean chloride ion concentrations at the three sites.

Table 5.13 Site pH Values

Date	Mean pH Values Top	Bottom	Bkg Top	Bkg Bottom
Site 1				
11/10/81	7.4	-	-	-
12/1/82	7.1	7.4	7.4	7.5
Site 2				
7/21/81	6.4	6.6	6.8	6.8
11/12/81	7.2	-	7.0	-
11/19/82	7.2	7.3	7.2	7.8
Site 3				
7/16/81	7.4	6.7	5.8	-
11/17/81	7.4	-	7.2	-
3/26/82	7.5	-	-	-

Table 5.14 Soil Chloride Concentration

Date	Mean Cl^- Concentration (mg/kg) Top	Bottom	Bkg T	Bkg B
Site 1				
6/30/82	119.6	103.3	17.6	15.4
Site 2				
7/8/82	28.0	33.1	13.7	2.9
Site 3				
11/4/82	72.6	101.5*	19.8	7.3

* Mean of 2 determinations

TOTAL ORGANIC CARBON

The average Total Organic Carbon (TOC) values for the sites are given in Table 5.15. The TOC values of the top (0-25 cm) of soil at sites 1 and 3 were significantly greater than background. The bottom (25-51 cm) sample at site 3 was also greater than background. At site 2 the top sample of 11/12/81 was significantly greater than background top sample. Sites with higher oil content have correspondingly high TOC values. These TOC values were determined using the Walkley-Black dichromate oxidation method taken from "Methods of Soil Analysis" edited by Black et al.. The oil at site 3 extended well below the zone of incorporation, hence the high TOC values of the bottom sample at site 3. There was not nearly as much penetration of oil at sites 1 and 2, hence the relatively low TOC values of the bottom samples from these sites.

The raw pH, chloride and TOC data is presented in Appendix C, Tables C-3, C-4 and C-5.

Table 5.15 Soil T.O.C.

Date	Mean TOC % Top	Bottom	Bkg T	Bkg B
Site 1				
11/10/81	10.4	1.5*	2.0	1.3
Site 2				
7/21/81	3.6	2.6	1.1	0.5
11/12/81	5.2	0.9	0.8	0.3
Site 3				
11/17/81	11.2	6.7	1.4	0.3

* Mean of 2 values

SOIL CHARACTERISTICS

The soil at the sites was characterized with respect to the following parameters:

(a) texture

(b) permeability

(c) x-ray diffraction

(d) cation exchange capacity.

Composite samples were collected from each site, as well as from areas adjacent to the sites. The samples from adjacent areas were analyzed to provide background data by which to evaluate any changes which had taken place.

Gradation Analysis

Grain size distributions for the soils were determined in accordance with ASTM Designation D422-63(72) (AASHTO Designation T-88-78). The deflocculating agent used was calgon solution. Further dispersion of clay particles was accomplished by applying a 10 psi air pressure from the Iowa dispersion jet for 5 minutes. Grain size distribution tests were run on the fraction of soil passing sieve #10 (2mm). For soils with oil contamination it was not possible to run the hydrometer test, because it was not possible to read the hydrometer correctly while oil was covering it. Interference from the oil occurred even after the samples had been subjected to

extraction with freon and dichloromethane for 24 hours.

Analyses were performed on soil samples taken from areas adjacent to the sites, and these resulted in the following classifications.

Site	Classification
Site 1	Silty loam
Site 2	Sandy loam
Site 3	Clay

Permeability

Permeability tests were conducted on samples of background soil, as well as composite samples of the top 25 cm. of site soil at each of the three sites. Due to the inconvenience in locations and time constraints, in situ permeability testing was not performed. Instead, soil samples from the sites were collected and standard laboratory permeability tests were run. Since the soils are classified as clay loams a modification of the constant head permeability test (AASHTO Designation: T 215-70, ASTM Designation: D 2434-68 (1974)) was used. The contact head method is preferred over the falling head method for such fine-grained soils because of the relatively low permeability coefficients obtained.

The procedure was modified somewhat from the stan-

dard method in that a nitrogen cylinder was used to create the pressure head instead of the contact head filter tank. In this way it was possible to control the amount of pressure used to make the water permeate the soil matrix and maintain laminar flow. Before testing began the optimum moisture content for each sample was determined from a standard proctor test (AASHTO Designation: T-99). Water was then added to each sample to bring it up to optimum moisture. The soils were compacted into the permeameter mould, and tap water was added on top. The soils were left to saturate for 48 hours. At the end of the 48 hours the pressure was turned on. The volume of water collected per time was recorded and the coefficient of permeability was calculated. The samples on which these permeabilities were determined were composite samples taken from the top 25 cm. of soil. The results are shown in Table 5.16.

No significant differences between the permeability of the background and site soil was observed at sites 1 and 3.

Table 5.16 Site Permeability Values

Site/Location	Permeability (water) (cm/sec)
Site 1 - Background	9.6×10^{-8}
Site 1 - Site Soil	5.03×10^{-8}
Site 2 - Background	-
Site 2 - Site Soil	1.3×10^{-6}
Site 3 - Background	1.95×10^{-7}
Site 3 - Site Soil	0.91×10^{-7}

X-Ray Diffraction

Composite samples of site soil and background soil were subjected to x-ray diffraction analyses. These analyses were performed using a Phillips Electronics APD 3600 Automated Power diffractometer. A comparison of the site soil patterns with those of background, revealed that some changes had taken place in the site soil structure.

Site 2

Soil samples from the site and one background sample were analyzed. The crystallinity of the soil samples did not change significantly in the site samples when compared to background. The decrease in intensity of the montmorillonite and chlorite peaks was more pronounced as the oil content increased. A possible explanation for this is that oil penetration into the interplanar layers of the minerals masked the effect of the crystalline materials. The calcite peak increased in intensity.

Site 1

The same trend as was observed at site 2 is observed here. Again the calcite peak increased in intensity.

Site 3

The general trend of decreased peak intensities with increased oil content is again evident here, with the exception once again of the calcite peak, which increased in intensity in one sample and decreased in intensity in

the other.

Generally, the major peaks either remained the same or diminished in intensity with increasing oil content. The exception to this trend was the calcite peak, which generally increased in intensity with increasing oil content. The x-ray diffraction spectra are shown in Appendix D.

Cation Exchange Capacity

The cation exchange capacity of the site soil and background was determined using the ammonium saturation method. The CEC of the top 25 cm. - zone of incorporation - was determined. The results reveal that at sites 1 and 2, there was generally an increase in CEC where oil was applied to the soil. However, at site 3, the CEC of site soil was slightly lower than that of the background soil. The CEC values of the site soil are listed in Table 5.17.

Table 5.17 Cation Exchange Capacity of Site Soil

Location	CEC (m.equivs./100g)
Site 1	
Area 1	15.4
Area 3	16.4
Area 6	19.5
Background	15.0
Site 2	
Area 6 - Untilled	14.6
Area 6 - Tilled	14.5
Area 3	7.0
Background	7.1
Site 3	
Area 2	12.1
Area 3	14.1
Area 4	13.6
Background	14.9

CHAPTER 6

EXTRACTION PROCEDURE TOXICITY OF SITE SOIL

The site soil from the three sites was subjected to the Extraction Procedure Toxicity test to determine

(1) whether or not the soil should be classified as hazardous.

(2) If there was any correlation between the concentration of pollutants in the extract and soil pore water. Several soil samples from each site were subjected to the extraction procedure, and then the extract was analyzed for metals and priority pollutants. The base/-neutrals and phenolics listed in Table 5.1 were evaluated in the E.P. extract. Table 6.1 lists the pollutants which were found in the E.P. extract from each site.

At site 1, four top and four bottom samples were analyzed, as well as 2 background samples. Only 1 top and 1 bottom sample showed any organics present, and the only compound shown to be present was phenol.

Five (5) top and 5 bottom samples were analyzed from site 2, as well as background top and bottom samples. In

Table 6.1 Priority Pollutants in Extraction Procedure Toxicity Extract

Compound	Concentration (ppm) Top	Bottom	# of +ve* values	# of samples analyzed
Site 1				
Phenol	.023	2.07	2	8
Site 2				
Phenol		15.06 115.97 41.58 1.93	4	10
Pentachlorophenol		7.61	1	10
Site 3				
Phenol	.053 .002		2	10
4-nitrophenol	.283 <.001		2	10
Pentachlorophenol	.078		1	10
Butylbenzyl-phthalate	<.078		2	10
Bis(2-ethylhexyl)-phthalate	<.001 <.001		2	10

* # of +ve values ≡ No. of samples yielding the compound

this case, two compounds were identified, phenol and pentachlorophenol. The samples which yielded pollutants were taken from the 25-50 cm layer, and corresponded to the areas of the site with the highest oil content.

Site 2 provided the highest percentage of samples yielding pollutants, with four of the ten samples extracted showed the presence of organics.

The only compound found in samples from all three sites was phenol.. Pentachlorophenol was found at two sites and 4-nitrophenol at one site. Traces of butylbenzylphthalate and Bis(2-ethylhexyl)phthalate were found at site 3, at a concentration of less than 1 ppb. None of the six pesticides and herbicides listed in the contaminants to be evaluated in the E.P. Toxicity procedure was found in the extracts from the three sites.

Table 6.2 lists the concentration of the metals Ag, Al, Ba, Cd, Cr, Cu, Ni, Pb, Zn and As found in the E.P. Toxicity extract of soil samples taken from the three sites. The extraction procedure was carried out on top (0-25 cm.) and bottom (25-50 cm.) samples at sites 1 and 2, and top samples only at site 3. Table 6.3 lists the compounds that must be present in an E.P. extract, and their concentrations, for the waste to be classified as hazardous. If the E.P. extract contains the contaminants listed at concentrations greater than or equal to the

Table 6.2 Metal Concentrations in Extraction Procedure Toxicity Extract

Location	Metals (mg/l)							
	Ag	Al	Cd	Cr	Cu	Ni	Pb	Zn
Site 1								
Bkg T	.020	0.47	.030	.050	<.002	<.01	0.18	9.60
1T	<.001	<.02	<.001	<.010	<.002	<.01	<.02	0.04
3T	.010	<.02	<.001	<.010	.040	<.01	<.02	2.22
4T	<.001	1.09	<.001	<.010	.280	.14	.07	4.80
6T	.020	<.02	<.001	<.010	<.002	<.01	<.02	1.66
1B	.020	<.02	<.001	.040	<.002	<.01	<.02	0.33
3B	<.001	<.02	<.001	<.010	<.002	<.01	<.02	0.06
4B	.050	0.30	<.001	<.010	.240	<.01	<.02	0.56
6B	<.001	<.02	<.001	.030	<.002	<.01	<.02	2.18
Site 2								
3T	<.001	<.02	<.001	.110	.020	.110	<.02	1.13
4T	.008	1.01	<.001	<.003	.020	.056	.12	3.90
6TT	<.001	1.63	<.001	.010	<.002	.048	.10	4.16
6TU	<.001	1.50	<.001	<.003	<.002	.048	.05	4.06
3B	<.001	<.02	<.001	.020	.002	<.008	<.02	<.01
4B	<.001	1.71	<.001	.010	<.002	.025	.05	2.04
6BT	<.001	1.19	<.001	.070	<.002	.033	.02	1.80
6BU	<.001	0.68	<.001	.010	<.002	.034	<.02	0.10
Bkg T	<.001	<.02	<.001	.040	<.002	<.008	.29	0.02
Bkg B	<.001	<.02	<.001	<.003	<.002	<.008	.17	<.01
Site 3								
Bkg T	.009	11.19	.001	<.003	.010	.100	.09	1.57
2T	<.002	6.33	<.001	.010	<.002	.036	.02	1.01
3T	.009	10.35	.016	.040	<.002	.113	.07	2.79
5T	.009	12.77	<.001	<.003	.010	.159	.12	2.79

Table 6.3 Maximum Concentration of Contaminants for Characteristics of E.P. Toxicity

Contaminant	Maximum Concentration (mg/l)
Arsenic	5.0
Barium	100.0
Cadmium	1.0
Chromium	5.0
Lead	5.0
Mercury	0.2
Selenium	1.0
Silver	5.0
Endrin (1,2,3,4,10,10- Hexachloro-1 7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1 4-endo, endo-5,8-dimethanonaph-thalene)	0.02
Lindane (1,2,3,4,5,6- Hexachlorocyclohexane, gamma isomer)	0.4
Methoxychlor (1,1,1-Trichloro-2,2-bis (p-methoxyphenyl) ethane)	10.0
Toxaphene ($C_{10}H_{10}Cl_8$, Technical chlorinated camphene, 67-69% chlorine)	0.5
2,4-D (2,4-Dichlorophenoxyacetic acid)	10.0
2,4,5-TP (Silvex) (2,3,5-Trichlorophenoxypropionic acid)	1.0

listed values, then the waste is said to exhibit the characteristic of E.P. Toxicity. It can be seen that the E.P. extract from the sites did not contain any of the listed compounds at critical concentrations.

Al, Cu, Ni and Zn were also determined on the E.P. extract. Zinc was present at concentrations up to 4.8, 4.2 and 2.8 mg/l at site 1, 2, and 3, respectively. However, these concentrations were all below the secondary maximum contamination levels for public water systems, and so posed no problem.

Aluminum levels in the extract from sites 1 and 2 were all below 2 mg/l, but the extract from site 3 contained high aluminum levels in the extract from both the site soil and the background sample. There are no drinking water standards for aluminum, and it is not generally considered a public health problem.

Copper levels in the extracts were almost all below the .002 mg/l detection limit for copper. The highest concentrations were found in one location at site 1, and the value was 0.280 mg/l. The secondary MCL for copper is 1 mg/l. Thus, to be significant in the extract, the concentration would need to exceed 100 mg/l. The other element examined, nickel, was also present in low concentrations. No MCL values are given for nickel in the primary or secondary water quality standards.

Table 6.4 shows E.P. extract metal concentrations

Table 6.4 Metals Concentration in E.P Toxicity Extract

Location	Metals mg/l Ag	Al	Cd	Cr	Cu	Ni	Pb	Zn
Site 1								
1T	.02	0.80	< .001	.060	.081	.349	0.25	5.00
3T	.01	2.20	< .001	.040	.138	.298	0.13	3.10
6T	.01	0.60	< .001	.020	.031	.169	0.10	2.80
Site 2								
1T	<.002	1.10	< .001	.010	.019	.190	.03	1.30
2T	<.002	1.20	< .001	.010	.007	.418	< .02	0.60
3T	<.002	1.70	< .001	.010	.046	.069	.10	1.20
4T	<.002	5.40	< .001	.040	.017	.124	< .02	0.60
5T	<.002	3.90	< .001	.020	.023	.083	.07	1.40
6T	<.002	1.60	< .001	.010	.005	.074	.08	1.20
Site 3								
1T	<.002	7.50	< .001	.010	.016	.091	.04	0.50
3T	<.002	3.70	< .001	.030	.008	.101	.06	1.00
4T	<.002	6.10	< .001	.020	.002	.078	.05	0.80

from another round of extractions on site soil. These extractions were carried out in the first year of the project, and extractions in Table 6.2 were carried out in the second year. The metal concentrations were again all below the levels necessary for the waste to be said to exhibit the characteristic of E.P. toxicity. Again the metals present in the highest concentrations were aluminum and zinc. However no metals were present at levels which exceeded the primary or secondary dirnking water standards.

Discussion

The results of the E.P. Toxicity procedure show that land treatment sites for oily residues are not hazardous with respect to E.P. Toxicity. Only five organic compounds were detected in the extract from the sites, with all five occurring at site 3 which had the highest oil content levels. Phenol occurred at all three sites, and in quite high concentrations at site 2. This does not necessarily mean that site 2 contained more phenol, since the different soil types at the sites may leach at different rates, and release different amounts of organics. Another point of interest is that all of the organics found at site 2 were found in the extract from the 25-50 cm. zone. Since site 2 had not had any residues applied for about six years when these samples were taken, this indicated some vertical movement of these

organic compounds had taken place. At site 1, even though phenol was found in the extract of a sample from 0-25 cm., the concentration in the 25-50 cm. sample was much higher.

Even though the site soil was not hazardous with respect to E.P. Toxicity, it could still be classified as hazardous. This is because of the presence of several compounds in the soil, such as benzo(a)pyrene, dibenzo-(a,h)anthracene, benzene, etc., which are classified as hazardous.

CHAPTER 7

UNSATURATED ZONE MONITORING

The unsaturated zone at each of the three sites was monitored for evidence of the presence of pollutants. The objective was to determine whether or not pollutants were migrating below the zone of incorporation. This monitoring was accomplished by taking core samples below the zone of incorporation at depths between 51 cm and 152 cm (20-60 inches), and by collecting samples of the soil pore water passing through the unsaturated zone using soil moisture samplers.

The soil core and soil pore water samples were analyzed for:

(1) oil content (2) heavy metals

(3) organics

In addition to these tests, some soil pore water samples were analyzed for:

(1) chloride

(2) pH

(3) conductivity

(4) C.O.D./T.O.C.

SOIL PORE WATER ANALYTICAL RESULTS

Priority Pollutants

Samples of soil pore water were analyzed for the B/N and phenolics as listed in Table 5.1. Samples from site 1 indicated the presence of 5 organic compounds in the soil water. These compounds were phenol, bis(2-ethylhexyl) phthalate, di-n-butylphthalate, butylbenzylphthalate and chrysene. Bis(2-ethylhexyl)phthalate showed up at concentrations of 120.8 and 55.64 mg/l in two samples. Three samples of soil pore water from site 1 were analyzed.

At site 2, a total of 5 samples were analyzed for priority pollutants, with only two samples showing the presence of any. The compounds found were phenol, chlorophenol and pentachlorophenol, all present at levels of less than 1 ppt. Only 1 sample of those analyzed at site 3 showed any organics present, and this was at a concentration of less than 1 ppt.

Background soil pore water samples were analyzed from sites 2 and 3, and no priority pollutants were found in these samples. No background soil water samples were obtained from site 1. Table 7.1 lists the priority pollutants compounds identified at the sites. The concentrations of the compounds identified at the sites are given in Tables B-5 to B-7, Appendix B.

TABLE 7.1 Priority Pollutants Present in Soil Pore Water

Compound	Site 1	Site 2	Site 3
Phenol	x	x	x
4-Nitrophenol		x	
Pentachlorophenol		x	
Chrysene	x		
Bis(2-ethylhexyl)phthalate	x		
Di-n-butylphthalate	x		

Metals

Tables 7.2 - 7.4 show the concentrations of metals found in the soil pore water. At site 1, barium was present in some samples at levels greater than the drinking water standards, but much lower than concentrations allowed for EP Toxicity extracts. Arsenic was present in two samples from one sampler at levels near the drinking water standard of 0.05 mg/l. Iron and manganese were present at quite high concentrations. Iron concentrations ranged from 0.20 to 11.99 mg/l, while manganese concentrations ranged from 0.12 to 12.00 mg/l.

At site 2, most metal concentrations in the site soil pore water samples were a little higher than those in the background soil pore water samples. However, with the exception of a few values for barium, zinc, iron and manganese, the concentrations were not higher than the drinking water standards, and all were lower than the EP Toxicity Standards. Barium concentrations of 3.82 and 4.63 mg/l were found in two samples collected from the same sampler at the site. As with site 1 samples, the values of iron were elevated, ranging from 0.09 to 4.44 mg/l, with a background value of 0.49 mg/l. The manganese values ranged from <0.01 to 34.60 mg/l. The 34.6 value seemed very high, but duplicate analyses yielded similar values.

At site 3, as with the other sites, only the barium,

Table 7.2 Soil Pore Water (mg/l) Metals (Site 1)

	Ag	Al	As	Ba	Cd	Cr	Cu	Ni	Pb	Zn	Fe	Mn
6/14/82												
Area 1	.008	.06	.042	5.28	<.001	.060	0.02	.04	<.02	1.44	5.81	1.70
Area 3	.011	.71	<.001	.58	<.001	.060	0.01	.028	<.02	.35	0.20	.12
Area 6	.010	.04	-	1.28	<.001	-	0.04	.036	<.02	.75	10.31	3.53
12/1/82												
Area 1	.011	.53	.089	2.13	<.001	.030	<.002	.035	<.02	2.44	4.62	1.32
Area 4	.011	0.80	.024	1.24	<.001	.060	.010	.035	<.02	.84	3.88	1.37
1/13/83												
Area 4	.021	0.09	-	2.15	-	.050	<.002	.08	0.20	.14	0.70	8.0
Area 6	.020	0.04	-	3.50	.001	.040	.01	.09	<.02	.04	11.99	12.00

Table 7.3 Soil Pore Water (mg/l) Metals (Site 2)

	Ag	Al	As	Ba	Cd	Cr	Cu	Ni	Pb	Zn	Fe	Mn
6/16/82												
Bkg	.006	0.58	<.001	.88	<.001	.050	.04	.001	<.02	<.001	.49	<.003
Area 6U	.009	0.85	0.140	.88	<.001	.070	.04	.023	<.02	0.73	4.44	34.600
Area 3	.013	0.42	.061	4.63	<.001	.030	.08	.048	<.02	1.04	.33	.006
Area 6T	.012	0.56	.028	.88	<.001	.030	.03	.015	<.02	4.34	.06	.253
11/19/82												
Area 5T	.012	0.59	.060	.70	<.001	.040	.06	<.001	<.02	0.07	1.38	1.090
4/11/83												
Area 3	.035	0.29	-	3.82	<.001	.030	.02	.50	0.44	0.08	.09	<.003

Table 7.4 Soil Pore Water (mg/l) Metals (Site 3)

	Ag	Al	As	Ba	Cd	Cr	Cu	Ni	Pb	Zn	Fe	Mn
6/15/82												
Bkg	.077	<.02	-	.77	<.001	.010	<.02	.208	.02	.49	.551	.463
Area 2	.022	.23	.054	2.53	<.001	.010	.02	.073	<.02	2.84	.964	7.31
Area 5	.044	.26	-	6.63	<.001	.040	.04	.429	<.02	.74	3.594	32.40
3/8/83												
Bkg	.026	.28	-	.62	<.001	.010	.05	.34	<.02	.08	.060	.01
Area 2	.043	.35	-	4.32	<.001	.070	.02	.40	<.02	.08	2.090	20.19

zinc, iron and manganese values were significantly higher than background. The manganese values were particularly high, with two different samples from the same area giving concentrations of 7.31 and 20.19 mg/l. Another sample from a different area, contained 32.4 mg/l of manganese.

pH

At site 1 only one set of pH values was obtained and these were all around 7. At site 2 the pH values of samples, taken at different times, ranged from 6.4 to 7.4. At site 3, pH values of soil water taken at different times again ranged from 6.4 to 7.4.

Chloride ion

The chloride ion concentration of the soil pore water at the sites is shown in Table 7.5. The concentrations at sites 1 and 3 were appreciably higher than the concentrations at site 2. The results indicated a decrease in the chloride ion concentration with time, with the sites with higher oil concentrations having higher chloride ion concentrations.

This shows that sites with high oil loading rates can leach significant amounts of chloride ion for a considerable period of time. No oil had been applied to site 2 since 1976, and the chloride ion concentration was low, while at sites 1 and 3, where the chloride ion was much higher, oil had been applied at high loading rates

Table 7.5 Soil Pore Water

Chloride Ion Concentration (mg/l)

Site 1

Date	Location			
	Area 1	Area 3	Area 4	Area 6
6/14/82	655.1	600.5	-	701.0
8/4/82	-	522.3	-	-
12/1/82	395.6	-	-	-
1/13/83	-	-	372	364.9

Site 2

Date	Location				
	Bkg	Area 3	Area 5	Area 6 (untilled)	Area 6 (tilled)
6/16/82	14.6	82.1	-	137.9	61.9
7/8/82	13.2	52.8	11.5	65.8	21.8
11/19/82	-	-	-	-	24.9
2/16/83	-	-	20.5	30.8	-
4/11/83	-	21.7	-	-	-

Site 3

Date	Location			
	Bkg	Area 2	Area 4	Area 5
6/15/82	112.8	1056.4	-	5147.4
10/19/82	-	759.0	-	-
3/3/83	40.9	486.5	-	-
6/7/83	28.7	434.9	-	2129.3

- No sample obtained on this date or no analysis performed because of insufficient sample

up until the beginning of 1981.

C.O.D./T.O.C.

The soil pore water contained oxidizable material at quite high levels when compared to backgound. At site 1, the C.O.D. values ranged from 400 mg/l to 2420 mg/l when the first C.O.D. samples were analyzed. Six months later, the highest concentration was 1690 mg/l. T.O.C. values were consistently lower than C.O.D. values, by a factor of about 3. Three T.O.C. values taken from one location at this site, indicated a decrease in T.O.C. with time.

Site 2 showed similar trends, with a C.O.D./T.O.C. ratio of about 3:1. Again there was a decrease in the T.O.C. values with time. The C.O.D. values also decreased. The amount of organic carbon present was lower than at site 1, as would be expected from the lower oil content values at site 2. Values ranged from 335 mg/l to 990 mg/l for C.O.D. on the first set of samples with a backgound value of 13 mg/l.

Site 3 samples showed a general trend of increasing C.O.D. at the 2 locations where several samples were collected over a 12 month period. Again a C.O.D./T.O.C. ratio of approximately 3:1 was observed. Tables 7.6 - 7.8 present the pH, C.O.D., T.O.C. and conductivity values of soil pore water samples. This data is presented graphically in Figures 7.1 - 7.7.

Table 7.6 Soil Pore Water Characteristics
Site 1

Date	Location	pH	C.O.D. (mg/l as O_2)	T.O.C. (as C)	Conductivity (μmhos/cm at 25°C)
6/14/82	Area 1	7.2	1580	458	-
	Area 3	7.0	400	110	-
	Area 6	7.2	2420	751	-
12/1/82	Area 1	-	1000	306	-
	Area 4	-	1000	-	-
	Area 6	-	1690	503.1	-
1/13/83	Area 6	-	-	488.7	-

Table 7.7 Soil Pore Water Characteristics
Site 2

Date	Location	pH	C.O.D. (mg/l as O_2)	T.O.C. (as C)	Conductivity (µmhos/cm at 25°C)
6/16/82	Bkg	-	13.	8.0	-
	Area 3	7.2	990	303.0	-
	Area 6U	7.0	750	232.0	-
	Area 6T	6.9	335	102.0	-
7/8/82	Bkg	7.1	50	8.0	-
	Area 3	6.8	960	300.0	-
	Area 5	7.4	235	-	-
	Area 6U	6.8	665	198.0	-
	Area 6T	6.9	300	86.0	-
11/19/82	Area 6U	-	770	-	
	Area 6T	-	460	-	
2/16/83	Area 3	6.6	-	243.3	2400
	Area 5	6.4	-	84.6	900
	Area 6U	6.6	-	187.5	2000
4/11/83	Area 3	6.8	560	212.4	-
	Area 5	6.5	325	108.8	-

Table 7.8 Soil Pore Water Characteristics
Site 3

Date	Location	pH	C.O.D. (mg/l as O_2)	T.O.C. (as C)	Conductivity (μmhos/cm at 25°C)
6/15/82	Bkg	6.8	93	41	-
	Area 2	7.3	440	117	-
	Area 4	6.6	850	204	-
10/19/82	Area 2	7.0	615	-	-
	Area 5	6.4	740	-	-
3/8/83	Bkg	7.0	90	32.8	1020
	Area 2	7.3	610	189.9	1700
	Area 5	-	630	-	-
5/2/83	Bkg	6.4	60	27.1	-
	Area 2	6.6	1180	352.9	-
	Area 5	-	750	-	-
6/7/83	Bkg	6.8	125	23.7	1000
	Area 2	6.8	1220	383.3	3500
	Area 5	7.4	850	-	-

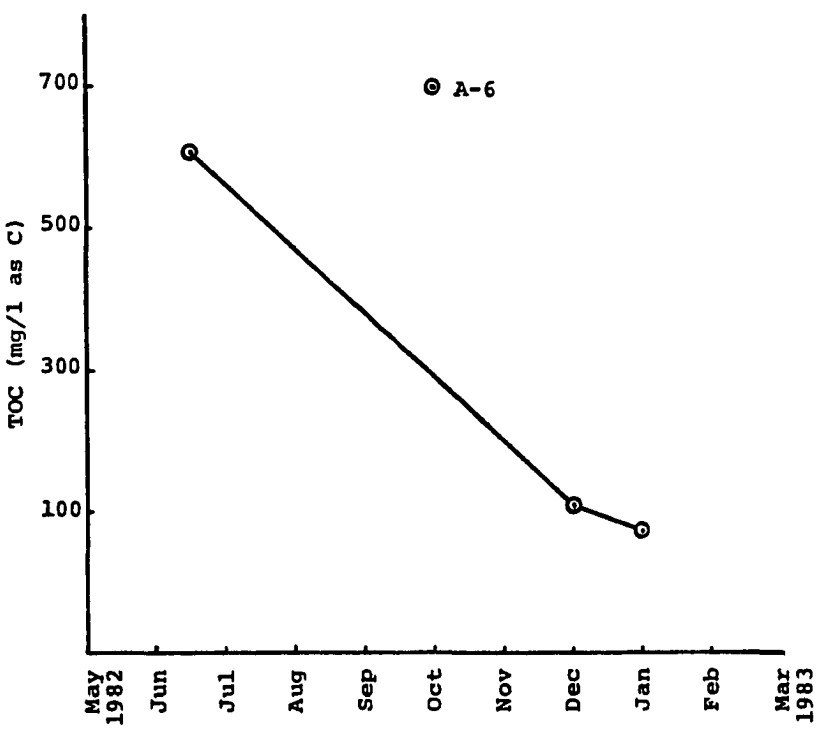

Figure 7.1 Graph of T.O.C. vs time for site 1 soil moisture samples

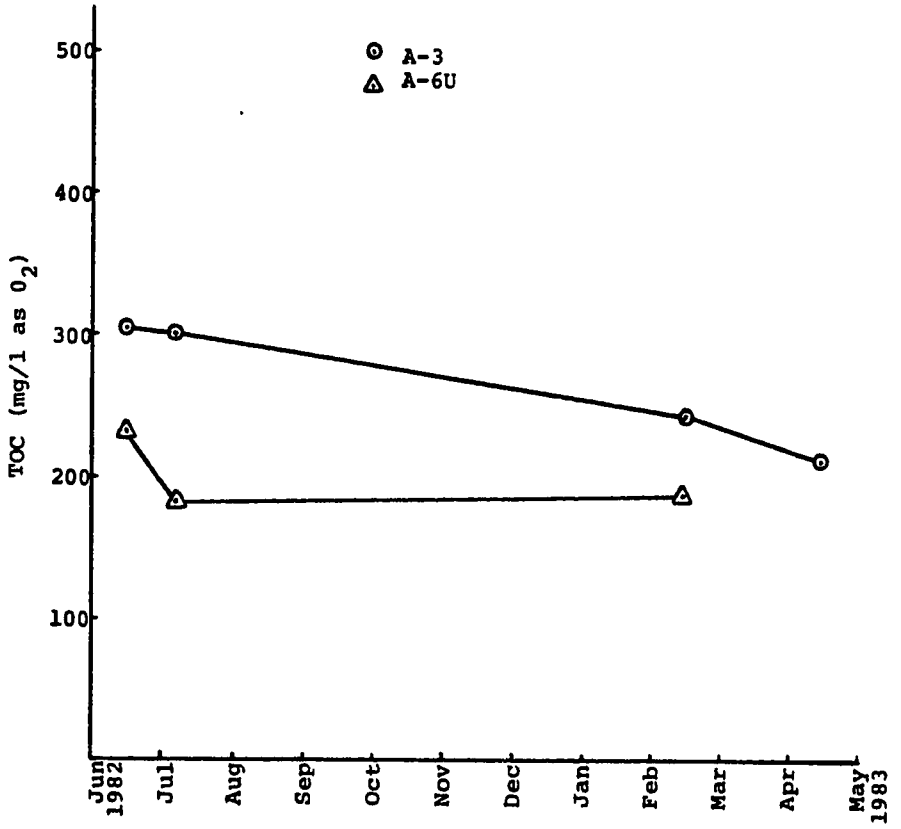

Figure 7.2 Graph of T.O.C. vs time for site 2 soil moisture samples

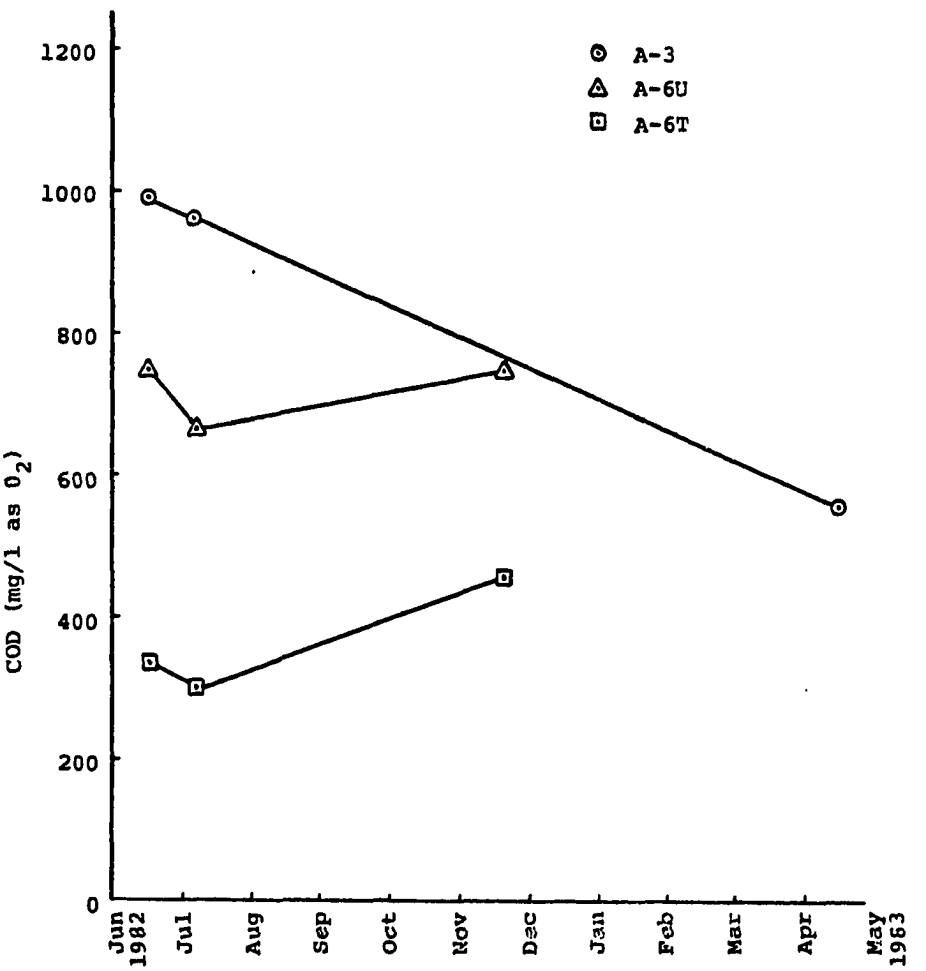

Figure 7.3 Graph of C.O.D. vs time for site 2 soil moisture samples

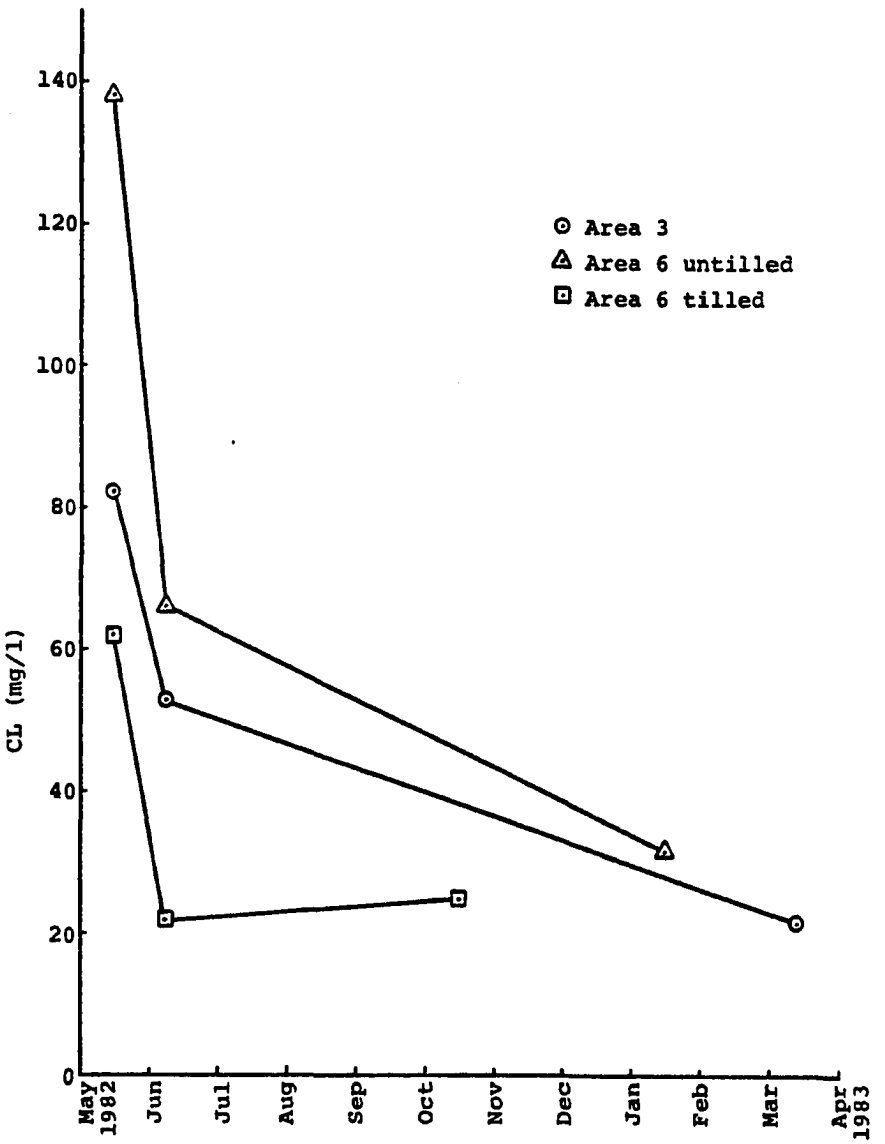

Figure 7.4 Graph of Cl vs time for site 2 soil moisture samples

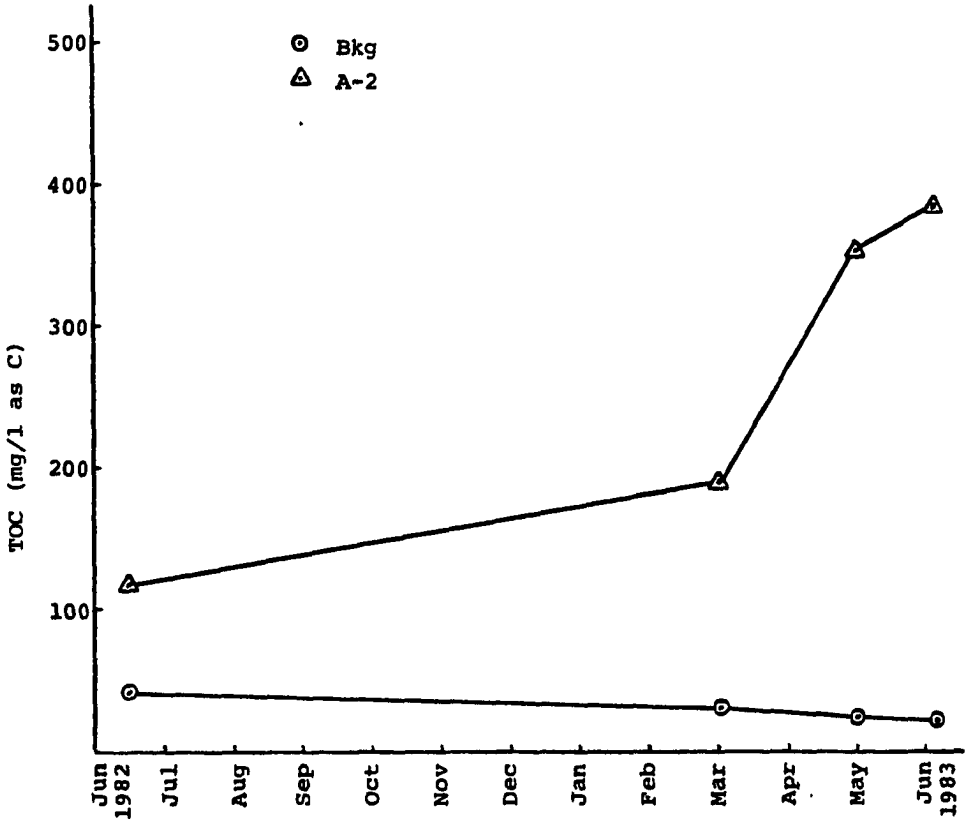

Figure 7.5 Graph of T.O.C. vs time for site 3 soil moisture samples

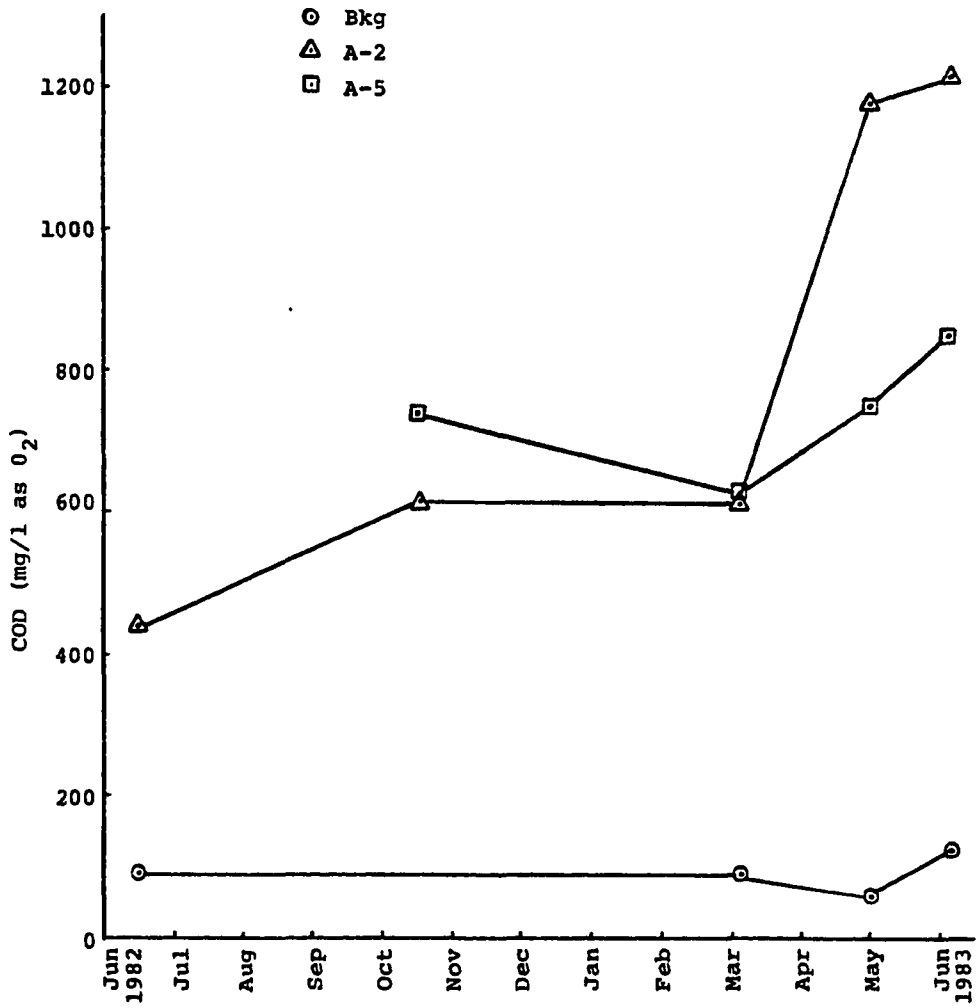

Figure 7.6 Graph of C.O.D. vs time for site 3 soil moisture samples

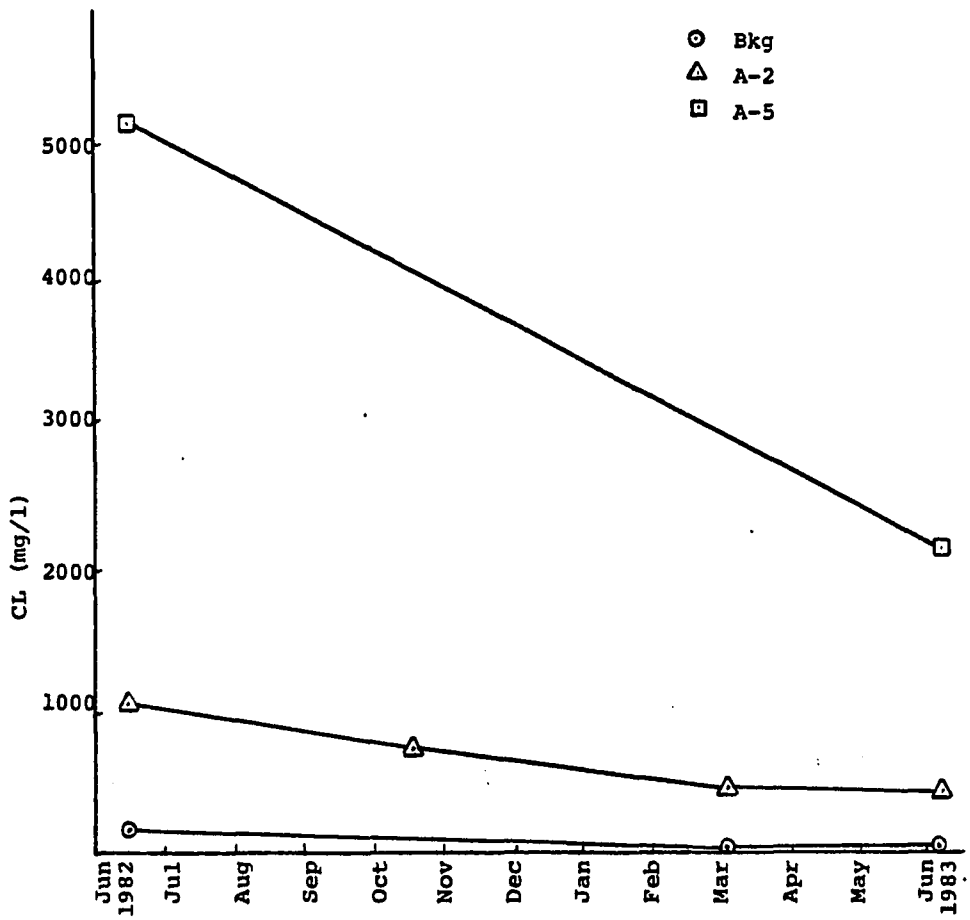

Figure 7.7 Graph of Cl vs time for site 3 soil moisture samples

Oil Content

Table 7.9 shows oil content values for some soil pore water samples from each of the three sites. There does not appear to be much correlation between the oil content and the T.O.C./C.O.D. values for the soil pore water. The sample from area 3 at site 2 had an oil content of 0.8 mg/l and a T.O.C. of 2433 mg/l, while the sample from area 6 at site 1, had an oil content of 133.2 mg/l and a T.O.C. of 488.7 mg/l.

The values show that oil can be leached from the top layers of the soil for some time after application of residues has ceased at a site.

Table 7.9 Oil Content of Soil Pore Water

Site No.	Location	Date	Oil Content (mg/l)
1	Area 1	12/1/82	60.7
1	Area 6	12/1/82	73.0
1	Area 6	1/13/83	133.2
2	Bkg	7/8/82	<0.1
2	Area 3	2/16/83	0.8
2	Area 6 U*	2/16/83	71.4
3	Bkg	3/8/83	<0.1
3	Area 2	3/8/83	13.2

* U - untilled.

DEEP CORE ANALYTICAL RESULTS

Deep cores refer to samples taken below 51 cm. depth. These samples were analyzed for oil content, metals and priority pollutants as a part of the unsaturated zone monitoring program.

Oil Content

The oil content of the deep cores taken at the sites with the exception of 2 samples at site 2 and at site 1, were all less than 0.1%, indicating that no oil had migrated below 51 cm. At site 2, two samples from area 6 had oil content values of 0.21 and 0.24%. Site 2 was the most permeable of the 3 sites, and area 6 was the area at site 2 with the highest oil content. Thus, it is possible that oil might have reached the 124 cm. (49 inches) depth. The high value at site 1 was in area 1, which had the lowest oil content at the site. It appears that this value was an outlier, since all other concentrations were very low, and the permeability of the site soil was very low. The oil content data is presented in Table 7.10.

Priority Pollutants

A number of organic priority pollutants were identified in the core samples at the unsaturated zone at the three sites. Table 7.11 lists the compounds identified at the sites. No compounds were found at all three sites, only 5 were found at 2 sites, and all other compounds at only one site. Anthracene, 1,2-Diphenylhyrazine, Bis(2-ethylhexyl)phthalate, Butylbenzylphthalate and 2,4-Dichlorophenol were the compounds found at 2 sites.

Priority pollutants were also found in the background cores at the sites. 1,2-Diphenylhydrazine was

Table 7.10 Oil Content Data for Deep Cores

Date	Location/Depth(cm)	Oil Content(%)
Site 1		
12/30/81	2(114-127)	.02
	3(81-122)	.01
	6(81-104)	.03
6/30/82	Bkg(102-112)	.05
	Bkg(152-168)	.11
	1(127-141)	.74
	6(107-117)	.06
	6(152-163)	.05
Site 2		
12/21/81	3(66-76)	.03
	3(76-91)	.02
	3(91-102)	.02
	5(66-91)	.00
	5(124-152)	.00
	6(66-81)	.21
	6(81-124)	.24
	6(124-147)	.04
7/8/82	2(84-94)	.04
	4(86-102)	.03
	4(127-137)	.02
	6(127-147)	.02
	Bkg(76-107)	.07
	Bkg(142-157)	.04
Site 3		
12/28/81	2(76-91)	.03
	3(81-91)	.01
	5(69-76)	.02
6/29/82	Bkg(76-89)	.03
	Bkg(117-130)	.05
	2(114-122)	.02
	6(132-142)	.03

Table 7.11 Priority Pollutants Present in Unsaturated Zone Cores

Compound	Site 1	Site 2	Site 3
Acenaphthene	x		
1.2-Disphenylhydrazine	x	x	
2,4 Dinitrotoluene	x		
Anthracene		x	x
Bis(2-ethylhexyl)phthalate		x	x
Isophorone		x	
Acenaphthylene		x	
Fluorene		x	
Diethylphthalate		x	
Butylbenzylphthalate		x	x
2-Nitrophenol		x	
4-Nitrophenol		x	
2.4-Dichlorophenol		x	x
Phenol		x	
Phenanthrene			x
Pyrene			x
Chrysene			x
Benzo(a)anthracene			x
Benzo(b)fluoranthene			x
Benzo(k)fluoranthene			x
Benzo(a)pyrene			x
2,6-Dinitrotoluene			x
Di-n-butylphthalate			x

found at site 1 and phenol at site 3. Site 2 background cores contained 5 compounds. The area from which background cores were taken at site 2, was contaminated with oil after the project started. This may be the reason for some of the anomalous results obtained with background samples taken from this area.

Concentrations of the compounds identified in the analysis of the deep cores are given in Tables B-5 through B-8, Appendix B. These concentrations are not absolute, but represent rough guides, since no study on recoveries of organics from soil matrices was performed.

Metals

The metal concentrations in the deep cores were not significantly above background concentrations, except for the nickel concentrations in both the first set of cores from the (127-152) cm depth at site 1, and the first set of cores from the (114-142) cm depth at site 3. However, the concentrations were quite low, 33 and 49 mg/kg at site 1 and 3, respectively. Thus, it appears that no buildup of metals occurred in the unsaturated zone. The raw metal data is given in Table C-6, and the mean concentrations in Table C-7, in Appendix C.

Discussion of Results

Monitoring of the unsaturated zone at these three sites revealed some interesting facts. The water passing through the unsaturated zone contained high amounts of

chloride, and appreciable amounts of Freon extractable compounds (oil and grease). Some metals are apparently solubilized under the conditions which exist at these sites. Even though the pH of the soil pore water and the pH of the soil in the top 51 cm. (20 inches) were both above 6.5 (usually above 7.0), barium, zinc, iron and manganese were found at fairly high concentrations, especially iron and manganese, in the soil pore water. Further monitoring of soil pore water at land treatment sites is necessary to verify these results.

No evidence of migration of oil into the soil of the unsaturated zone (below 50 cm.) was found. However the results suggest that there is some movement of organic priority pollutants into the unsaturated zone. It must be stressed that the quantitative values presented for these priority polluants are intended as guides only, since no work on recovery of organics from soil matrices was performed. The deep soil cores contained more compounds than the soil pore water. Whether this may due to better recoveries from the soil matrices as opposed to the aqueous phase, or to the absence of these compounds in the aqueous phase has not been determined.

The soil pore water also showed levels of T.O.C. and C.O.D. much above background at all sites. However, it appears that the oxidizable material present may have a large inorganic component, since the T.O.C./C.O.D. values

at site 2 are in the same range as those at site 3, where the soil organic content is very much higher. If the oxidizable material were primarily organic, one would expect site 3 to have much higher TOC/COD values than site 2.

At site 2, where the soil moisture samplers were located under tilled and untilled sections of area 6, the T.O.C., C.O.D. and Cl^- concentrations, as presented in Figures 7.3-7.5, are higher under the untilled area than under the tilled area.

This suggests that tilling the soil does have the effect of reducing the concentration of substances in the soil pore water. This is probably because the permeability of the tilled area is increased, resulting in less leaching of the till zone by infiltrating water. This results in lower contaminant concentration in the soil pore water, since most of the contaminants are in the till zone.

A comparison was made between the quality of the soil pore water collected in the soil moisture samplers and the extract from the Extraction Procedure Toxicity test. Samples of soil pore water collected on a specific date were analyzed for metals and priority pollutants. Soil samples collected on the same date were also analyzed for these pollutants. The samples on which the E.P. Toxicity test was run were collected at a later

date. It was felt that the concentration of pollutants in the soil, especially metals, would not change significantly over a short period of time.

There was poor correlation between the concentration of metals in the soil pore water, and the concentration of metals in the E.P. Extract of both top and bottom soil samples or the concentration of metals in the soil cores. In calculating the correlation coefficient, the concentration values for all three sites were used. This was done because a general correlation between metal concentrations in soil cores, soil pore water and E.P. Extract was being evaluated. In addition, not enough data was available from individual sites to make valid correlations for each site. Table 7.12 presents a comparison of the metal concentrations in the E.P. Extract, soil pore water and soil samples. There was also poor correlation between the metal concentrations in the soil pore water and soil samples.

A quantitative comparison was not attempted with the organics, because of insufficient data. Table 7.13 tabulates the organic priority pollutants identified in soil pore water and E.P. Extracts from the three sites. The only compound that shows up in both types of samples is phenol. Not enough data is available to draw any conclusions about the ability of the E.P. Extract to simu-

Table 7.12 Comparison of Concentration of Metals in E.P. Extract, Soil Pore Water and Soil Samples

Metal	Concentration (ppm) Soil Pore Water	E.P. Toxicity Extract Top	E.P. Toxicity Extract Bottom	Soil Samples Top	Soil Samples Bottom
Site 1 - Area 1					
Ag	.008	<.001	.020	17.0	4.0
Al	.060	<.020	< .020	-	-
As	.042	-	-	-	-
Ba	.528	-	-	41.0	101.0
Cd	<.001	<.001	<.001	<1.0	<1.0
Cr	.060	<.010	.040	248.0	141.0
Cu	.020	<.002	<.002	101.0	76.0
Ni	.040	<.010	<.010	23.0	15.0
Pb	<.020	<.020	<.020	112.0	56.0
Zn	1.44	.040	.330	523.0	307.0
Site 1 - Area 4					
As	.011	<.001	.050	<3.0	<3.0
Al	.800	1.09	.300	-	-
As	.024	-	-	-	-
Ba	1.240	-	-	174.0	94.0
Cd	<.001	<.001	<.001	<1.0	<1.0
Cr	.060	<.010	<.010	70.0	38.0
Cu	.010	.250	.240	64.0	13.0
Ni	.035	.140	<.010	28.0	24.0
Pb	<.020	.070	<.020	75.0	20.0
Zn	.840	4.800	0.560	207.0	191.0

(continued)

Table 7.12 (continued)

Metal	Concentration (ppm) Soil Pore Water	E.P. Toxicity Extract Top	E.P. Toxicity Extract Bottom	Soil Samples Top	Soil Samples Bottom
Site 1 - Area 6					
Ag	.010	.010	<.001	7.0	3.0
Al	.040	<.020	<.020	-	-
As	-	-	-	-	-
Ba	1.280	-	-	122.0	86.0
Cd	<.001	<.001	<.001	<1.0	-
Cr	-	<.010	.030	337.0	45.0
Cu	.040	<.002	<.002	140.0	14.0
Ni	.036	<.010	<.010	32.0	17.0
Pb	<.020	<.020	<.020	79.0	10.0
Zn	.750	.330	2.180	431.0	64.0
Site 2 - Area 6 Untilled					
Ag	.009	<.001	<.001	<3.0	<3.0
Al	.85	1.50	.68	-	-
As	.140	-	-	-	-
Ba	.88	-	-	10.0	8.0
Cd	<.001	<.001	<.001	<1.0	<1.0
Cr	.070	<.003	.010	152.0	36.0
Cu	.040	<.002	<.002	30.0	10.0
Ni	.023	.048	.034	12.0	10.0
Pb	<.02	.05	<.02	60.0	11.0
Zn	.73	4.06	.10	160.0	69.0
Site 2 - Area 6 Tilled					
Ag	.012	<.001	<.001	<3.0	<3.0
Al	.56	1.63	1.19	-	-
As	.028	-	-	-	-
Ba	.88	-	-	18.5	13.5
Cd	<.001	<.001	<.001	<1.0	<1.0
Cr	.030	.010	.070	86.0	37.0
Cu	.300	<.002	<.002	13.0	13.0
Ni	.015	.048	.033	7.0	16.0
Pb	<.02	.10	.02	30.0	8.0
Zn	4.34	4.16	1.80	99.0	151.0

(continued)

Table 7.12 (continued)

Metal	Concentration (ppm) Soil Pore Water	E.P. Toxicity Extract Top	E.P. Toxicity Extract Bottom	Soil Samples Top	Soil Samples Bottom
Site 2 - Area 3					
Ag	.013	<.001	<.001	3.0	<3.0
Al	.42	<.02	<.02	-	-
As	.061	-	-	-	-
Ba	4.63	-	-	8.0	6.0
Cd	<.001	<.001	<.001	<1.0	<1.0
Cr	.030	.110	.020	40.0	27.0
Cu	.080	.020	.002	9.0	6.0
Ni	.048	.110	<.008	8.0	11.0
Pb	<.02	<.02	<.02	11.0	11.0
Zn	1.04	1.13	<.01	52.0	34.0
Site 3 - Area 2					
Ag	.022	<.002	-	<3.0	<3.0
Al	.23	6.33	-	-	-
As	.054	-	-	-	-
Ba	2.53	-	-	89.0	121.0
Cd	<.001	<.001	-	<1.0	<1.0
Cr	.010	.010	-	33.0	68.0
Cu	.020	<.002	-	16.0	6.0
Ni	.073	.036	-	19.0	21.0
Pb	<.02	.02	-	23.0	20.0
Zn	2.84	1.01	-	89.0	121.0
Site 3 - Background					
Ag	.077	.009	-	4.0	<3.0
Al	.02	11.19	-	17810	13500
As	-	-	-	-	-
Ba	0.77	-	-	-	-
Cd	<.001	.001	-	<1.0	<1.0
Cr	.010	<.003	-	20.0	30.0
Cu	<.020	.010	-	15.0	8.0
Ni	.208	.100	-	40.0	16.0
Pb	.02	.09	-	30.0	23.0
Zn	.49	1.57	-	5.0	-

(continued)

Table 7.12 (continued)

Metal	Concentration (ppm) Soil Pore Water	E.P. Toxicity Extract Top	Bottom	Soil Samples Top	Bottom
Site 3 - Area 5					
Ag	.044	.009	-	-	-
Al	.26	12.77	-	-	-
As	-	-	-	-	-
Ba	6.63	-	-	-	-
Cd	<.001	<.001	-	-	-
Cr	.040	<.003	-	-	-
Cu	.040	.010	-	-	-
Ni	.429	.159	-	-	-
Pb	<.02	.12			
Zn	.74	2.79	-	-	-

Table 7.13 Comparison of Priority Pollutants Present in Soil Pore Water and E.P. Extract

	Soil Pore Water	E.P. Extract
Site 1	Phenol Bis(2-ethylhexyl)phthalate Di-n-butylyphthalate Butylbenzylphthalate Chrysene	Phenol
Site 2	Phenol 4-Nitrophenol Pentachlorophenol	Phenol Pentachlorophenol
Site 3	Phenol	Phenol 4-Nitrophenol Pentachlorophenol Butylbenzyl-phthalate Bis(2-ethyhexyl)-phthalate

late the leaching of organics. However, the data presented indicatess that phenols will be extracted by the procedure.

CHAPTER 8

CONCLUSIONS

A number of conclusions can be drawn from the results of this study.

(1) The soil pore water passing through the unsaturated zone can contain high levels of salts, especially chloride, as well as high levels of iron and manganese. The high chloride levels apparently decrease with time, but persist for longer than the 90 days now required for monitoring soil pore water after waste application has ceased. Monitoring of the soil pore water for longer than 90 days is required.

(2) The addition of nutrients, especially nitrate, appears to be vital for the continued degradation of oily residues after closure. No significant degradation occurred at the sites during the study period, even though degradeable material was present at the sites.

(3) Some vertical migration of oil does occur at

land treatment sites, but this migration does not extend below 50 centimeters of the surface. Most metals are immobilized in the top 25 cm. of soil.

(4) Sampling procedures at land treatment sites must be carefully planned, to ensure that representative samples are obtained, since there is considerable variability in pollutant concentrations across land treatment sites.

(5) Organic compounds present in the soil at land treatment sites are primarily polynuclear aromatic compounds and phenols. Several of them were found in the unsaturated zone at the sites, but at very low concentrations (in the ppb range). This indicates that movement of pollutants into the unsaturated zone does occur.

(6) The soil at land treatment sites used for oily residue treatment, does not exhibit the characteristic of EP toxicity. However a few priority pollutants were identified in the EP extract from the sites. Phenol was the predominant compound identified, and was found in 8 of 30 samples analyzed. The site soil could still be classified as hazardous, since it contained compounds such as benzo(a)pyrene

which are hazardous.

(7) The E.P. Toxicity extract does not appear to model leachate at land treatment sites as far as metal content is concerned. There was no correlation between the concentration of metals in the soil pore water, and the concentration of metals in the E.P. Toxicity extract of soil from the same location. Organics identified in the extract were primarily phenolics.

(8) Tilling the soil at land treatment sites decreases the T.O.C., C.O.D. and Cl^- ion concentrations in the leachate.

(9) The treatment zone at land treatment sites is defined in the Federal Register (July 26, 1982) as the region from the soil surface down to a depth of 1.5 meters (5 feet). In addition, the bottom of the zone must be at least 1 meter (3 feet) above the seasonal high water table. The results of this experimental work show that this minimum depth above the water table is too shallow to prevent salts and solubilized metals from reaching the ground water. Furthermore, the oil which migrates below the aerobic zone (top 20-25 cm.), while immobilized, is not degraded and may act as a source of contaminated leachate.

RECOMMENDATIONS FOR FURTHER STUDY

The results of this study indicate the need for further research in several areas.

(1) There is need for more research on identifying organic compounds present at land treatment sites both qualitatively and quantitatively. A major component of any such work would have to be studies on the recovery of organics from soil matrices contaminated with oil.

(2) More work is needed on soil pore water monitoring at these sites. The effect of different methods of installation on the characteristics of the pore water sample needs to be evaluated, as well as the effect of the porous ceramic cup on pollutants in the soil pore water, especially organics.

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APPENDIX A

Quality Assurance/Quality Control Data

APPENDIX A

Table A-1 Blank Concentrations mg/l

	Cu	Ni	Zn	Ba	Cr	Al	Pb	As	Cd	Fe	Mn	Ag
Soil Pore Water												
Blank #1	.02	<.008	.46	.26	<.01	.20	.15	.108	<.01	.049	.007	.006
Blank #2	.03	<.008	.04	<.02	.05	.10	<.02	-	-	.090	.010	.014
E.P. Toxicity												
Blank #1	<.002	<.008	.31	.29	<.01	.22	<.02	-	.02	-	-	.03
Blank #2	.02	.130	.10	.20	.01	.35	.10	-	.01	-	-	<.002
Blank #3	.01	.015	.19	.28	.02	.29	<.02	-	<.01	-	-	.011
Blank #4	.01	.010	.16	-	.08	.20	.03	-	<.01	-	-	.010
Soil Samples												
Blank #1	<.002	<.008	.01	.11	<.01	-	<.02	-	<.01	-	-	.013
Blank #2	.01	.010	.03	.15	.08	-	.03	-	<.01	-	-	.010

TABLE A-2 List of Duplicate Determinations for Soil Samples Concentrations (mg/kg)

	Al	Ba	As	Cu	Cd	Ni	Pb	Zn	Cr	Ag	Co
2111281S											
1BT	12,410	-	33.0	10.0	<1.0	27.0	30.0	43.0	3.0	2.0	10.0
1BT	16,490	-	8.0	11.0	<1.0	26.0	37.0	42.0	<1.0	3.0	7.0
3111781S											
1B	15,800	-	333.0	15.0	<1.0	16.0	33.0	<1.0	43.0	4.0	10.0
1B	14,900	-	267.0	18.0	<1.0	18.0	47.0	<1.0	53.0	4.0	10.0
1063092S											
1(34-36)	-	250.6	-	9.0	<1.0	16.0	20.0	46.0	23.0	3.0	-
1(34-36)	-	165.0	-	9.0	<1.0	7.0	29.0	38.0	22.0	3.0	-
1123081S											
3(32-48)	31,170	-	-	3.0	<1.0	27.0	13.0	40.0	-	2.0	-
3(32-48)	32,000	-	-	8.0	<1.0	36.0	23.0	37.0	-	1.0	-
2070881S											
2(33-37)	-	16.0	-	3.0	<1.0	14.0	13.0	23.0	13.0	3.0	-
2(33-37)	-	83.0	-	6.0	<1.0	7.0	6.0	19.0	16.0	3.0	-
2122181											
6(49-58)	21,000	-	-	21.0	<1.0	35.0	3.0	33.0	-	5.0	-
6(49-58)	34,000	-	-	16.0	<1.0	39.0	10.0	37.0	-	2.0	-

(continued)

TABLE A-2 (continued)

	Al	Ba	As	Cu	Cd	Ni	Pb	Zn	Cr	Ag	Co
1061482S											
1T	-	41.0	-	202.0	<1.0	23.0	112.0	523.0	248.0	17.0	-
1T	-	630.0	-	215.0	<1.0	31.0	120.0	758.0	260.0	18.0	-
2061682S											
3T	-	8.0	-	9.0	<1.0	8.0	11.0	52.0	40.0	<1.0	-
3T	-	9.0	-	10.0	<1.0	13.0	15.0	96.0	33.0	<1.0	-
2111281S											
Bkg T	-	-	-	6.0	<1.0	8.0	17.0	26.0	<1.0	1.0	<0.5
Bkg T	-	-	-	9.0	<1.0	11.0	23.0	41.0	33.0	<1.0	7.0
4 TT	-	-	-	21.0	<1.0	58.0	47.0	94.0	70.0	6.0	7.0
4 TT	-	-	-	22.0	<1.0	84.0	60.0	106.0	60.0	3.0	3.0
3062982S											
4 T	-	133.0	-	43.0	<1.0	12.0	87.0	-	67.0	3.0	-
4 T	-	214.0	-	43.0	<1.0	20.0	80.0	-	60.0	3.0	-
1111081S											
2 B	24,220	-	340.0	32.0	4.0	27.0	33.0	73.0	57.0	5.0	10.0
2 B	25,140	-	370.0	33.0	<1.0	35.0	47.0	65.0	-	5.0	7.0
2111281S											
Bkg B	9,410	-	<8.0	6.0	<1.0	11.0	13.0	31.0	<1.0	1.0	3.0
Bkg B	10,940	-	<8.0	21.0	<1.0	23.0	13.0	50.0	20.0	3.0	7.0

Table A-3 Compounds Recovered from Spike

Base/Neutrals	Phenolics
1,3-Dichlorobenzene	2-Chlorophenol
1,4-Dichlorobenzene	Phenol
Hexachloroethane	2,4-Dichlorophenol
Hexachlorobutadiene	2-Nitrophenol
Naphthalene	p-chloro-m-cresol
Bis(2-chloroethyl)ether	2,4-Dimethylphenol
Hexacholorocylopentadiene	Pentachlorophenol
Nitrobenzene	
Bis(2-chloroethoxy)methane	
2-Chloronaphthalene	
Acenaphthene	
Isophorone	
Fluorene	
2,6-Dinitrotoluene	
Hexachlorobenzene	
Phenanthrene	
Anthracene	
Dimethylphthalate	
Diethylphthalate	
Fluoranthene	
Pyrene	
Di-n-buthyphthalate	
Butylbenzylphthalate	
Chrysene	
Bis(2-ethylhexyl)phthalate	
Benzo(a)anthracene	
Benzo(b)fluoranthene	
Benzo(k)fluoranthene	
Benzo(a)pyrene	
Indeno(1,2,3-cd)pyrene	

Table A-4 Compounds Not Recovered from Spike

Base/Neutrals	Phenolics
Acenaphthylene	2,4-Dinitrophenol
1,2-Dichlorobenzene	
1,2-Diphenylhydrazine	
4-Bromophenyl phenyl ether	
Benzidine	
Dibenzo(a,h)anthracene	
Benzo(g,h,i)perylene	

Table A-5 Compounds Identified in Duplicate Soil Samples

Compound	Sample 1	Sample 2
Sample code 1120182S		
Bis(2-ethylhexyl)phthalate	x	
Benzo(a)anthracene	x	
Benzo(b)fluoranthene	x	x
Benzo(a)pyrene	x	x
Dibenzo(a,h)anthracene	x	x
Benzo(g,h,i)perylene	x	x
Benzo(k)fluoranthene	x	x

Table A-6 Duplicate Oil Content Data

Location		% Oil
2040682S		
	2TU	2.5
	2TU	2.5
2070882S		
	1TU	3.1
	1TU	3.9
	1BU	1.6
	1BU	1.8
	2TU	4.8
	2TU	3.3
	2BU	0.9
	2BU	1.0
	3TU	2.4
	3TU	2.9
	3BU	1.9
	3BU	1.0
	4BU	1.1
	4BU	1.0
	5TU	3.7
	5TU	4.6
	5BU	1.2
	5BU	1.7
3060783S		
	5T	10.0
	5T	9.9
	5B	16.7
	5B	15.6
	6T	5.5
	6T	5.1
	Bkg T	2.0
	Bkg T	2.3

APPENDIX B

Concentrations of Priority Pollutants Identified

Table B-1 Priority Pollutants in Soil at Site 1

Compound	Concentration mg/kg					
	11/10/81		6/14/82		12/1/82	
	Top	Bottom	Top	Bottom	Top	Bottom
Benzo(b)fluoranthene		<.001			.010	.036
					62.4	
Benzo(k)fluoranthene		<.001		.036	.010	.036
					68.4	
Benzo(a)anthracene	78.80	<.001	.003	<.001	3.686	12.81
	1.976	<.001		.003		
	26.6					
	17.08 x 10^3					
	874.00					
Phenanthrene	.006	<.001	<.001	<.001		
	.003			<.001		
	.001	<.001				
	.012	<.001				
	<.091					
Fluoranthene	.012	<.001	<.001	<.001		
	.193			.001		
	14.700					
	.002					

(continued)

Table B-1 (continued)

Compound	Concentration mg/kg					
	11/10/81		6/14/82		12/1/82	
	Top	Bottom	Top	Bottom	Top	Bottom
Butylbenzylphthalate	.009 <.001 .104 .002 <.001	<.001 <.001	<.001	<.001 <.001		
Benzo(a)pyrene		4482. .332			.026 7.24	
Dibenzo(a,L)anthracene					<.001 135.9	.019
Benzo(g,h,i)perylene					.002 229.1	0.200
Anthracene	.006 .001 .002 .009 <.001	<.001 <.001	<.001 <.001	<.001 <.001		
Naphthalene	.053		<.001 <.001	<.001		

(continued)

Table B-1 (continued)

Compound	Concentration mg/kg					
	11/10/81		6/14/82		12/1/82	
	Top	Bottom	Top	Bottom	Top	Bottom
Benzene	.021					
	<.001					
	<.001					
	<.001					
Pyrene	3.142	<.001	<.001	.001		
	.358	<.001		<.001		
	9.594					
	14.924					
Toluene	<.001					
	.002					
	.011					
Ethylbenzene	<.001					
	<.001					
	<.001					
Di-n-butylphthalate						
Chyrsene			<.001	<.001	<.001	<.001
			<.001	.003		
Bis(2-ethyhexyl)phthalate	.073	<.001	<.001	<.001	<.001	<.001
	.006		<.001			
Isophorone			<.001			

(continued)

Table B-1 (continued)

Compound	Concentration mg/kg					
	11/10/81		6/14/82		12/1/82	
	Top	Bottom	Top	Bottom	Top	Bottom
Phenol	<.001	<.001	.0234	.1170	8.957	.1073
	.031		1.863		5.770	129.0
	<.001		.0141		42.980	
	<.001				30.700	
	<.001					
Pentachlorophenol	<.001					
	<.001					

Table B-2 Priority Pollutants in Soil at Site 2

Compound	Concentration mg/kg					
	9//81 or 11/12/81		6/16/82		11/19/82	
	Top	Bottom	Top	Bottom	Top	Bottom
Anthracene	.318	<.001	0.018			
	6.520					
	<.001					
	.578					
	11.772					
Benzene	<.001	<.001				
	<.001					
	<.001					
	<.001					
Naphthalene	.264		3.378			
	9.480		<.001			
	.425					
Phenanthrene	.318	<.001				
	6.520	13.630				
	0.578					
	11.772					
	<.001					
1,2-Diphenylhydrazine			.011	.001		
			0.448			
Isophorone	.090	.040				
	.222					

(continued)

Table B-2 (continued)

Compound	Concentration mg/kg					
	9//81 or 11/12/81		6/16/82		11/19/82	
	Top	Bottom	Top	Bottom	Top	Bottom
Bis(2-ethylhexyl)phthalate			<.001	<.001		4.068
Pyrene	.062 .072	.131				
Butylbenzylphthalate			<.001	<.001		
Phenol	<.001 <.001 <.001 <.001	.001 <.001	.027			
4-Nitrophenol						.0013
Pentachlorophenol	.260 <.001	<.001				.2814
2-Nitrophenol			.849			

Table B-3 Priority Pollutants in Soil at Site 3

Compound	Concentration mg/kg					
	11/17/81		6/29/82		10/19/82	
	Top	Bottom	Top	Bottom	Top	Bottom
Chrysene			<.001			
			<.001			
Benzo(a)anthracene			<.001		.002	.002
			.0002		1.421	
Bis(2-ethylhexyl)phthalate	.196		<.001		.012	
	.167		<.001			
Isophorone			<.001			
			<.001			
			<.001			
2,6-Dinitrotoluene	.806	1.586	<.001			
	4.53	.005				
	.038	.023				
	.052					
N-Nitrosodiphenylamine			<.001			
Dibenzo(a,h)anthracene					<.001	<.001
					.005	
					.016	
Benzo(a)pyrene					.095	

(continued)

Table B-3 (continued)

Compound	Concentration mg/kg					
	11/17/81		6/29/82		10/19/82	
	Top	Bottom	Top	Bottom	Top	Bottom
Fluoranthene	.091	2.059				
	.024					
Phenol					0.220	.288
					0.058	
Benzene	.034	<.001				
	<.001					
	<.001					
	.005					
Bromoform	<.001	<.001				
		<.001				
Toluene	1.079	.653				
	5.790					
Ethylbenzene	<.001	.003				
	.006	.001				

Table B-4 Compounds Present in Backgound Samples

Compound	Concentration in Background Sample (mg/kg) Top (0-25 cm)	Bottom (25-51 cm)
Site 1		
Chrysene	<.001	
Bis(2-ethylhexyl)phthalate	0.538	0.520
		.077
Benzo(b)fluoranthene		0.721
Benzo(k)fluoranthene	0.220	0.721
Benzo(a)anthracene	<.001	
Phenol		<.001
Site 2		
1,2-Diphenylhydrazine	<.001	<.001
Butylbenzylphthalate		<.001
Bis(2-ethylhexyl)phthalate	<.001	
Chrysene	.008	
Benzo(a)anthracene	.008	
2-Nitrophenol		0.102
4-Nitrophenol		.006
Site 3		
Ethylbenzene		.003
Bis(2-ethylhexyl)phthalate	<.001	0.801
	16.57	
Naphthalene	.002	
Isophorone	<.001	
Pyrene	.001	
Chrysene	<.001	
Benzo(a)anthracene	<.001	
Toluene	4.92	

Table B-5 Priority Pollutants Present in the Unsaturated Zone at Site 1

Deep Soil Cores

Compound	Concentration (mg/kg) Top	Bottom	# of +ve Observations
1,2-Diphenyl-hydrazine	.001	<.001	3
Acenaphthene		<.001	1
2,4-Dinitrotoluene	<.001	<.001	2

Soil Pore Water

Compound	Concentration (mg/l)	# of +ve Observations
Phenol	.122 .067 .052	3
Bis(2-ethylhexyl)-phthalate	120.80 55.64	2
Di-n-butylphthalate	.031	1
Butylbenzylphthalate	.036	1
Chrysene	.631	1

Table B-6 Priority Pollutants Present in the Unsaturated Zone at Site 2

Deep Soil Cores

Compound	Concentration (mg/kg) Top	Bottom	# of +ve Observations
1,2-Diphenylhydrazine	.010	.010 .056	3
Anthracene	<.001	-	1
Bis(2-ethylhexyl)-phthalate	<.001 .008	-	2
Isophorone	<.001		1
Acenaphthylene		<.001	1
Fluorene	<.001	<.001	2
Diethylphthalate	<.001	-	1
Butylbenzylphthalate	<.001	-	1
2-Nitrophenol	0.676	-	1
4-Nitrophenol	0.384	-	1
2,4-Dichlorophenol	0.010	-	1
Phenol	0.089	0.138	2

Soil Pore Water

Compound	Concentration (mg/l)	No. of +ve Observations
Phenol	<.001	1
4-Nitrophenol	<.001	1
Pentachlorophenol	<.001	1

Table B-7 Priority Pollutants Present in the Unsaturated Zone at Site 3

Deep Soil Cores

Compound	Concentration (mg/kg) Top	Bottom	# of +ve Observations
Anthracene	-	1.28	1
Phenanthrene	1.32	16.90	2
Pyrene	1.17	13.16	2
Di-n-butylphthalate	.352 4.76	-	2
Butylbenzylphthalate	12.02 650.90	80.80	3
Chrysene	0.284	3.49	2
Bis(2-ethylhexyl) phthalate	6.19 140.5	8.87	3
Benzo(a) anthracene	0.396	3.76	2
Benzo(b) fluoranthene	.056	-	1
Benzo(k) fluoranthene	.044	-	1
Benzo(a) pyrene	0.394	-	1
2,4-Dichlorophenol	0.069	-	1
2,6-Dinitrotoluene	0.515	-	1
Soil Pore Water			
Phenol	< .001		1

Table B-8 Priority Pollutants Found in the Background Samples of the Unsaturated Zone

Compound	Concentrations (mg/kg) Top	Bottom
Site 1		
1,2-Diphenylhydrazine	0.040	-
Site 2		
1,2-Diphenylhydrazine	-	.001
Anthracene		<.001
Bis(2-ethylhexyl)phthalate		<.001
2-Nitrophenol	1.166	-
4-Nitrophenol	0.662	.097
Site 3		
Phenol	-	0.273

APPENDIX C

Site Soil Data

Table C-1 Oil Content Data %

Site 1	Location	Date							
		9/3/81	11/10/81	4/8/82	6/14/82	6/30/82	8/4/82	12/1/82	1/18/83
	BGT	0.8	0.1	0.3	0.5	-	-	0.5	1.0
	1TU	2.3	2.5	4.4	6.6	-	-	6.9	5.9
	1BU	3.8	0.1	0.7	1.9	0.7	-	1.5	-
	2TU	-	1.7	7.1	-	-	5.8	7.7	8.2
	2BU	-	0.1	0.8	-	8.0	1.0	1.2	-
	3TU	1.5	1.2	3.4	2.5	3.6	2.3	2.9	-
	3BU	1.0	0.3	-	0.1	0.3	0.2	0.6	-
	4TT	2.5	-	4.0	-	5.5	-	4.7	-
	4BT	0.1	-	0.4	-	0.1	-	0.7	-
	5TT	3.4	1.2	6.5	8.0	-	7.1	8.3	7.9
	5BT	-	-	1.1	-	-	1.5	3.0	-
	6TT	3.1	1.2	4.0	4.0	6.2	-	3.2	5.8
	6BT	0.2	0.4	0.2	0.1	0.1	-	4.1	-
	BGB	-	0.0	0.1	0.1	-	-	0.2	-

(continued)

Table C-1 (continued)

Site 2	Location	Date					
		11/12/81	4/6/82	7/8/82	11/19/82	6/16/82	2/16/83
	BGT	0.0	0.3	3.7	0.4	3.1	0.6
	BGB	0.0	0.1	0.5	0.4	0.3	-
	1TT	1.7	2.8	2.4	3.3	-	3.0
	1BT	0.3	1.4	1.1	-	-	-
	1TU	0.8	3.8	3.1	3.1	-	-
	1BU	0.2	-	1.6	1.0	-	-
	2TT	-	2.5	3.0	2.1	-	2.6
	2BT	-	0.5	1.5	1.3	-	-
	2TU	1.5	2.5	4.8	0.1	-	-
	2BU	0.3	-	1.0	0.1	-	-
	3TT	-	1.6	1.7	1.8	.5	1.7
	3BT	0.2	0.6	0.6	0.1	0.1	-
	3TU	1.4	3.3	2.9	1.1	-	-
	3BU	0.1	-	1.9	0.2	-	-
	4TT	0.2	1.7	1.8	1.2	-	0.7
	4BT	0.0	0.4	1.0	0.3	-	-
	4TU	1.9	2.8	0.4	3.7	-	-
	4BU	0.3	0.5	1.1	2.8	-	-
	5TT	-	4.2	4.0	4.7	-	5.1
	5BT	-	1.0	1.2	3.0	-	-
	5TU	1.0	2.9	3.7	3.6	-	-
	5BU	0.4	-	1.2	2.1	-	-
	6TT	-	3.0	-	4.5	0.2	4.7
	6BT	-	0.8	-	2.6	0.1	1.7
	6TU	1.0	2.4	0.7	4.3	1.3	-
	6BU	0.2	0.5	0.2	0.3	0.2	-

(continued)

Table C-1 (continued)

Site 3	Location	Date						
		11/17/81	3/26/82	7/29/82	10/19/82	11/4/82	3/8/83	6/7/83
	BGT	0.2	0.1	-	0.5	-	1.1	2.3
	BGB	0.1	0.1	-	0.1	-	-	0.1
	1T	3.0	5.3	-	-	-	-	4.0
	1B	-	0.1	-	-	-	-	0.5
	2T	2.0	5.6	-	5.2	-	-	5.7
	2B	0.9	0.2	-	-	-	-	0.9
	3T	8.6	10.5	-	-	-	11.0	9.3
	3B	3.5	0.2	-	-	-	-	1.4
	4T	4.9	8.4	13.2	13.9	-	15.3	14.1
	4B	6.1	2.3	2.4	17.9	-	-	8.6
	5TT	4.6	9.6	17.3	13.1	13.4	20.8	15.6
	5BT	2.4	10.7	6.2	5.9	-	-	9.9
	6T	-	12.8	12.5	-	11.9	12.0	9.4
	6B	-	-	8.7	-	-	-	9.5

TABLE C-2 SOIL METALS DATA (mg/kg)

SITE 1

SITECODE	ID *	BA	SE	AS
10702815	1(0-6)	.	.	.
	1(6-12)	.	.	.
	2(0-6)	.	.	.
	2(6-9)	.	.	.
	3(0-8)	.	.	.
	4(0-8)	.	.	.
	4(7-12)	.	.	.
	5(0-10)	.	.	.
	6(0-8)	.	.	.

CU	CD	CR	NI
183.00	0.00	22.00	314.00
129.00	0.00	.	29.00
274.00	1.00	.	42.00
141.00	0.00	23.00	75.00
246.00	0.00	.	43.00
250.00	0.00	22.00	137.00
18.00	0.00	16.00	75.00
316.00	0.00	28.00	82.00
246.00	1.00	.	37.00

PB	ZN	AL	CR
97.00	323.00	17790.00	126.00
65.00	240.00	.	88.00
151.00	514.00	.	203.00
83.00	170.00	29300.00	107.00
291.00	554.00	.	232.00
93.00	580.00	21360.00	317.00
10.00	50.00	31650.00	7.00
137.00	583.00	20210.00	350.00
95.00	660.00	.	360.00

AG	MN	FE
15.00	.	.
.	.	.
.	.	.
13.00	.	.
.	.	.
24.00	.	.
2.00	.	.
30.00	.	.
.	.	.

* Area (depth in inches)

(continued)

TABLE C-2 (continued)

SITE 1

SITECODE	ID	BA	SE	AS
10702815	BGD(0-6)	•	•	•
	BGB	•	•	340.00

	CU	CD	CU	NI
	18.00	0.00	16.00	117.00
	11.00	4.00	7.00	19.00

	PB	ZN	AL	CR
	23.00	10.00	•	•
	27.00	20.00	20600.00	37.00

	AG	MN	FE
	4.00	•	•
	1.00	0.00	•

(continued)

TABLE C-2 (continued)

SITE 1

SITECODE	ID	BA	SE	AS
11110815	1B	.	.	400.00
	1B	.	.	270.00
	1T	.	.	440.00
	2B	.	.	340.00
	2B	.	.	370.00
	2T	.	.	270.00
	3T	.	.	340.00
	5T	.	.	400.00
	6T	.	.	270.00

CU	CD	CO	NI
19.00	1.00	7.00	23.00
21.00	4.00	13.00	20.00
180.00	0.00	7.00	44.00
32.00	4.00	10.00	27.00
33.00	1.00	7.00	35.00
143.00	4.00	17.00	231.00
154.00	4.00	7.00	57.00
187.00	1.00	10.00	44.00
50.00	5.00	7.00	28.00

PB	ZN	AL	CR
43.00	46.00	23160.00	53.00
43.00	61.00	18660.00	0.00
137.00	489.00	16710.00	270.00
33.00	73.00	24220.00	57.00
67.00	65.00	25140.00	0.00
93.00	274.00	18230.00	110.00
100.00	272.00	12880.00	157.00
123.00	443.00	13170.00	140.00
57.00	195.00	18840.00	90.00

AG	MN	FE
2.00	.	.
3.00	.	.
17.00	0.00	.
5.00	0.00	.
5.00	0.00	.
17.00	.	.
14.00	0.00	.
17.00	0.00	.
0.00	0.00	.

(continued)

TABLE C-2 (continued)

SITE 1

SITECODE	ID	BA	SE	AS
10614825	BGT	90.00	.	.
	BGB	94.00	.	.
	1T	41.00	.	.
	1B	101.00	.	.
	3T	174.00	.	.
	3B	94.00	.	.
	6T	122.00	.	.
	6B	86.00	.	.
	1T	630.00	.	.

CU	CD	CD	NI
13.00	1.00	.	13.00
9.00	1.00	.	16.00
202.00	1.00	.	23.00
76.00	1.00	.	15.00
64.00	1.00	.	28.00
13.00	1.00	.	24.00
140.00	1.00	.	32.00
14.00	.	.	17.00
215.00	1.00	.	31.00

PB	ZN	AL	CR
30.00	121.00	.	30.00
17.00	64.00	.	33.00
112.00	523.00	.	248.00
56.00	307.00	.	141.00
75.00	207.00	.	70.00
20.00	191.00	.	38.00
79.00	431.00	.	337.00
10.00	64.00	.	45.00
120.00	758.00	.	260.00

AG	MN	FE
3.00	.	.
3.00	.	.
17.00	.	.
4.00	.	.
3.00	.	.
3.00	.	.
7.00	.	.
3.00	.	.
18.00	.	.

(continued)

TABLE C-2 (continued)

SITE 2

SITECODE	ID	BA	SE	AS
20721815	1(0-6)	•	•	•
	1(6-12)	•	•	•
	1(12+)	•	•	•
	2(0-8)	•	•	•
	2(8+)	•	•	•
	3(0-8)	•	•	•
	3(8+)	•	•	•
	4(0-8)	•	•	•
	4(8-16)	•	•	•

CU	CD	CD	NI
76.00	0.00	22.70	60.00
17.70	0.00	21.00	38.00
23.30	0.00	27.00	46.00
59.70	1.30	24.70	56.00
33.00	0.00	30.70	84.00
283.00	0.00	25.70	44.00
23.30	0.00	29.70	54.00
88.70	0.00	23.70	57.00
23.70	0.00	24.30	56.00

PB	ZN	AL	CR
113.00	208.00	23140.00	270.00
50.00	65.00	20700.00	127.00
25.00	19.00	11650.00	73.00
53.00	89.00	36370.00	140.00
35.00	87.00	42330.00	137.00
47.00	74.00	25270.00	77.00
27.00	44.00	29850.00	87.00
197.00	377.00	30000.00	460.00
133.00	160.00	28390.00	223.00

AG	MN	FE
7.00	•	•
5.00	•	•
3.00	•	•
5.00	•	•
6.00	•	•
4.00	•	•
4.00	•	•
10.00	•	•
7.00	•	•

(continued)

TABLE C-2 (continued)

SITE 2

SITECODE	ID	BA	SE	AS
20721815	5(0-8)	.	.	.
	5(8+)	.	.	.
	6(0-8)	.	.	.
	6(8+)	.	.	.
	BGT	.	.	.
	BGB	.	.	.

CU	CD	CD	NI
22.30	0.30	29.70	70.00
11.70	0.00	29.30	104.00
15.00	0.00	21.00	29.00
18.70	0.00	22.30	41.00
18.30	0.00	14.00	35.00
14.00	0.00	17.00	50.00

PB	ZN	AL	CR
30.00	70.00	25210.00	73.00
20.00	22.00	30970.00	70.00
13.00	0.00	14000.00	53.00
23.00	9.00	16710.00	73.00
20.00	19.00	13780.00	27.00
17.00	12.00	13990.00	43.00

AG	MN	FE
5.00	.	.
3.00	.	.
1.00	.	.
5.00	.	.
4.00	.	.
3.00	.	.

(continued)

TABLE C-2 (continued)

SITE 2

SITECODE	ID	BA	SE	AS
21112815	1BT	•	•	33.00
	1TT	•	•	0.00
	1BU	•	•	0.00
	1TU	•	•	0.00
	1BT	•	•	0.00
	2TU	•	•	0.00
	2BU	•	•	67.00
	3BU	•	•	67.00
	3TU	•	•	0.00

CU	CD	CU	NI
10.00	0.00	10.00	27.00
24.00	0.00	0.00	12.00
14.00	0.00	7.00	42.00
38.00	0.00	10.00	29.00
11.00	0.00	7.00	26.00
22.00	0.00	3.00	45.00
9.00	0.00	10.00	20.00
6.00	0.00	10.00	15.00
35.00	0.00	7.00	21.00

PB	ZN	AL	CR
30.00	43.00	12420.00	3.00
77.00	141.00	10500.00	93.00
17.00	45.00	16230.00	20.00
113.00	175.00	13000.00	167.00
37.00	42.00	10490.00	0.00
47.00	167.00	6700.00	67.00
10.00	49.00	10400.00	0.00
20.00	33.00	10100.00	0.00
97.00	130.00	11440.00	193.00

AG	MN	FE
2.00	0.00	•
4.00	0.00	•
0.00	0.00	•
5.00	0.00	•
3.00	0.00	•
3.00	0.00	•
0.00	0.00	•
2.00	0.00	•
3.00	0.00	•

(continued)

TABLE C-2 (continued)

SITE 2

SITECODE	ID	BA	SE	AS
21112815	48T	.	.	0.00
	4TT	.	.	67.00
	4TT	.	.	0.00
	4BU	.	.	0.00
	4TU	.	.	0.00
	5BU	.	.	0.00
	5TU	.	.	0.00
	8GB	.	.	0.00
	8GT	.	.	0.00

CU	CD	CU	NI
11.00	3.00	7.00	128.00
21.00	0.00	7.00	58.00
22.00	0.00	3.00	84.00
13.00	2.00	7.00	28.00
44.00	0.00	7.00	27.00
15.00	0.00	10.00	17.00
32.00	0.00	7.00	19.00
0.00	0.00	3.00	11.00
0.00	0.00	0.00	8.00

PB	ZN	AL	CR
27.00	84.00	11850.00	17.00
47.00	94.00	10670.00	70.00
60.00	106.00	11120.00	60.00
23.00	52.00	17770.00	50.00
120.00	188.00	10960.00	157.00
27.00	41.00	21400.00	27.00
70.00	100.00	13350.00	170.00
13.00	31.00	9410.00	0.00
17.00	26.00	6360.00	0.00

AG	MN	FE
1.00	0.00	.
0.00	0.00	.
3.00	0.00	.
16.00	0.00	.
0.00	0.00	.
3.00	0.00	.
4.00	0.00	.
1.00	0.00	.
1.00	0.00	.

(continued)

TABLE C-2 (continued)

SITE 2

SITECODE	ID	BA	SE	AS
21112d15	BGB	.	.	0.00
	BGT	.	.	0.00
	BBJ	.	.	0.00
	BTJ	.	.	0.00

CU	CD	CD	NI
21.00	0.00	7.00	23.00
9.00	0.00	7.00	11.00
14.00	1.00	7.00	22.00
33.00	3.00	13.00	29.00

PB	ZN	AL	CR
13.00	50.00	10940.00	20.00
23.00	41.00	8610.00	33.00
30.00	59.00	19860.00	43.00
113.00	162.00	17000.00	137.00

AG	MN	FE
3.00	0.00	.
0.00	0.00	.
4.00	0.00	.
3.00	0.00	.

(continued)

TABLE C-2 (continued)

SITE 2

SITECODE	ID	BA	SE	AS
20016625	BGT	5.00	.	.
	BGB	3.50	.	.
	3T	8.00	.	.
	3b	6.00	.	.
	6TU	10.00	.	.
	6BU	8.00	.	.
	6TT	18.50	.	.
	6BT	13.50	.	.
	3T	9.00	.	.

CU	CD	CO	NI
7.00	1.00	.	8.00
4.00	1.00	.	22.00
9.00	1.00	.	8.00
6.00	1.00	.	11.00
30.00	1.00	.	12.00
10.00	1.00	.	10.00
13.00	1.00	.	7.00
13.00	1.00	.	16.00
10.00	1.00	.	13.00

PB	ZN	AL	CR
16.00	68.00	.	18.00
10.00	67.00	.	17.00
11.00	52.00	.	40.00
11.00	34.00	.	27.00
60.00	160.00	.	152.00
11.00	69.00	.	36.00
30.00	99.00	.	86.00
8.00	151.00	.	37.00
15.00	96.00	.	33.00

AG	MN	FE
3.00	.	.
3.00	.	.
3.00	.	.
3.00	.	.
3.00	.	.
3.00	.	.
3.00	.	.
3.00	.	.
3.00	.	.

(continued)

TABLE C-2 (continued)

SITE 3

SITECODE	ID	BA	SE	AS
31117815	1B	.	.	333.00
	1S	.	.	267.00
	1T	.	.	0.00
	2B	.	.	133.00
	2T	.	.	167.00
	3B	.	.	0.00
	3T	.	.	33.00
	4B	.	.	100.00
	4T	.	.	67.00

CU	CD	CO	NI
15.00	0.00	10.00	16.00
18.00	0.00	10.00	18.00
28.00	0.00	13.00	22.00
11.00	0.00	13.00	18.00
8.00	0.00	7.00	19.00
32.00	0.00	3.00	40.00
53.00	0.00	10.00	199.00
58.00	0.00	0.00	24.00
44.00	0.00	10.00	17.00

PB	ZN	AL	CR
33.00	0.00	15800.00	43.00
47.00	0.00	14900.00	53.00
64.00	35.00	18400.00	110.00
40.00	00.00	10850.00	60.00
20.00	0.00	10020.00	40.00
70.00	32.00	22550.00	67.00
117.00	174.00	22220.00	97.00
130.00	97.00	24200.00	23.00
93.00	62.00	20030.00	23.00

AG	MN	FE
4.00	0.00	.
4.00	0.00	.
4.00	0.00	.
2.00	0.00	.
3.00	0.00	.
6.00	0.00	.
7.00	0.00	.
8.00	0.00	.
6.00	0.00	.

(continued)

TABLE C-2 (continued)

SITE 3

SITECODE	ID	BA	SE	AS
31117813	SS	.	.	0.00
	ST	.	.	167.00
	BGB	.	.	0.00
	BGT	.	.	0.00

CU	CD	CD	NI
29.00	0.00	10.00	48.00
58.00	0.00	3.00	40.00
8.00	0.00	13.00	16.00
15.00	0.00	7.00	40.00

PB	ZN	AL	CR
70.00	65.00	23960.00	50.00
160.00	86.00	22910.00	63.00
23.00	0.00	13500.00	30.00
30.00	5.00	17810.00	20.00

AG	MN	FE
3.00	0.00	.
9.00	0.00	.
2.00	0.00	.
4.00	0.00	.

(continued)

TABLE C-2 (continued)

SITE 3

SITECODE	ID	BA	SE	AS
30629825	1T	59.00	.	.
	1B	67.00	.	.
	4T	133.00	.	.
	4B	56.00	.	.
	2T	89.00	.	.
	2B	121.00	.	.
	3T	213.00	.	.
	3B	42.00	.	.
	4T	214.00	.	.

CU	CD	CD	NI
10.00	1.00	.	8.00
10.00	1.00	.	18.00
43.00	1.00	.	12.00
15.00	1.00	.	22.00
10.00	1.00	.	19.00
6.00	1.00	.	21.00
30.00	1.00	.	16.00
12.00	1.00	.	28.00
43.00	1.00	.	20.00

PB	ZN	AL	CR
13.00	59.00	.	36.00
13.00	67.00	.	44.00
87.00	133.00	.	67.00
30.00	56.00	.	71.00
23.00	89.00	.	46.00
20.00	121.00	.	33.00
96.00	213.00	.	88.00
15.00	42.00	.	37.00
60.00	214.00	.	80.00

AG	MN	FE
3.00	.	.
3.00	.	.
3.00	.	.
3.00	.	.
3.00	.	.
3.00	.	.
4.00	.	.
3.00	.	.
3.00	.	.

Table C-3 Soil pH

Site 1

Location	pH	
	11/10/81	12/1/82
Bkg T	-	7.4
Bkg B	-	7.5
1T	7.2	7.1
1B	-	7.5
2T	7.6	7.0
2B	-	7.5
3T	7.4	7.2
3B	-	7.3
4T	-	7.1
4B	-	7.3
5T	7.2	7.0
5B	-	7.5
6T	7.5	7.1
6B	-	7.2

Site 2

Location	pH		
	7/21/81	11/12/81	11/19/82
Bkg T	6.8	7.0	7.2
Bkg B	6.8	-	7.8
1T	6.9	7.0	7.0
1B	7.9	-	7.2
2T	6.2	7.1	7.4
2B	5.8	-	7.3
3T	6.2	7.3	7.3
3B	5.8	-	7.6
4T	6.7	7.3	7.3
4B	7.3	-	7.4
5T	6.1	7.2	7.2
5B	6.2	-	6.8
6T	6.4	7.4	7.1
6B	6.3	-	7.2

(continued)

Table C-3 (continued)

Site 3

Location	pH		
	7/16/81	11/17/81	3/26/82
Bkg T	5.8	7.2	-
1T	7.5	7.4	7.7
1B	7.2	-	-
2T	7.4	7.4	7.1
2B	6.6	-	-
3T	7.2	-	7.5
3B	6.8	-	-
4T	7.6	7.3	7.3
4B	6.0	-	-
5T	7.3	7.4	7.6
5B	7.3	-	-
6T	-	-	7.6
6B	-	-	-

Table C-4 Chloride Ion Concentration (mg/kg)

Site 1

Date	Location	Concentration (mg/kg) (1:5 ratio)*	(1:1 ratio)*
6/30/82	Bkg T	17.6	5.5
	Bkg B	15.4	-
	1T	167.0	-
	1B	136.1	103.9
	2T	161.5	-
	2B	112.1	93.5
	3T	68.1	-
	3B	70.4	58.0
	4T	108.8	-
	4B	87.4	85.7
	5T	106.6	-
	5B	130.5	109.9
	6T	105.5	-
	6B	83.5	69.8

* Ratio of soil to water

Site 2

Date	Location	Concentration (mg/kg) (1:1 ratio)*	(1:5 ratio)*
7/8/82	Bkg T	13.7	47.8
	Bkg B	2.9	17.6
	1TU	24.9	52.7
	1BU	28.1	-
	2TU	24.9	19.8
	2BU	45.1	-
	3TU	19.0	22.8
	3BU	-	-
	4TU	28.2	33.9
	4BU	23.9	-
	5TU	34.3	37.5
	5BU	35.4	-
	6TU	36.9	24.2
	6BU	-	-

* Ratio of soil to water

(continued)

Table C-4 (continued)

Site 3

Date	Location	Concentration (mg/kg) (1:5 ratio)*	(1:1 ratio)*
11/4/82	Bkg T	19.8	15.4
	Bkg B	7.3	4.1
	2T	48.5	17.2
	4T	125.1	99.6
	4B	150.4	141.7
	5T	71.7	51.1
	5B	52.5	49.2
	6T	44.9	52.1

* Ratio of soil to water

Table C-5 Total Organic Carbon

Site 1

Location	T.O.C. %
	11/10/81
Bkg T	2.0
Bkg B	1.3
1T	10.0
1B	0.9
2T	10.2
2B	2.1
3T	13.4
5T	13.6
6T	4.9

Site 2

Location	T.O.C. %	
	7/21/81	11/12/81
Bkg T	1.1	0.8
Bkg B	0.5	0.3
1T	4.2	4.8
1B	3.9	0.1
2T	4.1	4.0
2B	1.3	0.2
3T	4.1	5.3
3B	1.8	0.3
4T	6.7	5.5
4B	7.2	1.3
5T	1.7	6.9
5B	1.0	1.9
6T	0.7	4.6
6B	0.6	1.3

(continued)

Table C-5 (continued)

Site 3

Location	T.O.C. %
	11/17/81
Bkg T	1.4
Bkg B	0.3
1T	7.6
1B	1.4
2T	1.7
2B	1.1
3T	14.6
3B	8.8
4T	13.6
4B	11.7
5T	18.4
5B	10.7

TABLE C-6 DEEP CORES METALS DATA

SITE 1

SITECODE	ID *	BA	BE	AS
11230815	2(45-50)	.	.	.
	2(50-60)	.	.	.
	3(32-48)	.	.	.
	3(32-48)	.	.	.
	6(32-41)	.	.	.
	6(45-50)	.	.	.
	BGD(30-42)	123.00	.	.
	BGD(50-62)	58.00	.	.

CU	CD	CO	NI
14.00	0.00	.	38.00
6.00	0.00	.	27.00
3.00	0.00	.	27.00
8.00	0.00	.	36.00
9.00	0.00	.	44.00
24.00	0.00	.	40.00
8.00	3.00	.	22.00
14.00	3.00	.	11.00

PB	ZN	AL	CR
13.00	40.00	33830.00	.
20.00	43.00	29170.00	.
13.00	40.00	31170.00	.
23.00	37.00	32000.00	.
20.00	30.00	27670.00	.
17.00	50.00	27500.00	.
18.00	44.00	.	26.00
17.00	46.00	.	29.00

AG	MN	FE
5.00	.	.
1.00	.	.
2.00	.	.
1.00	.	.
4.00	.	.
7.00	.	.
3.00	.	.
4.00	.	.

* Area (depth in inches)

(continued)

TABLE C-6 (continued)

SITE 1

SITECODE	ID	BA	SE	AS
10e30e25	eGD(30-42)	125.00	.	.
	DGD(56-62)	58.00	.	.
	1(34-36)	250.00	.	.
	1(50-55)	54.00	.	.
	e(30-35)	63.00	.	.
	e(49-55)	43.00	.	.
	1(34-36)	165.00	.	.

CU	CD	CG	NI
8.00	3.00	.	22.00
14.00	3.00	.	11.00
9.00	3.00	.	16.00
9.00	3.00	.	33.00
9.00	3.00	.	17.00
9.00	3.00	.	11.00
9.00	3.00	.	7.00

PB	ZN	AL	CR
18.00	44.00	.	26.00
17.00	46.00	.	29.00
20.00	46.00	.	23.00
6.00	51.00	.	60.00
36.00	49.00	.	30.00
10.00	85.00	.	26.00
29.00	38.00	.	22.00

AG	MN	FE
3.00	.	.
4.00	.	.
3.00	.	.
5.00	.	.
3.00	.	.
3.00	.	.
3.00	.	.

(continued)

TABLE C-6 (continued)

SITE 2

SITECODE	ID	BA	SE	AS
2122181	3(26-30)	.	.	.
	3(30-36)	.	.	.
	3(36-40)	.	.	.
	5(26-36)	.	.	.
	5(36-49)	.	.	.
	5(49-60)	.	.	.
	6(26-32)	.	.	.
	6(32-49)	.	.	.
	6(49-58)	.	.	.

CU	CD	CD	NI
18.00	3.00	.	24.00
6.00	0.00	.	25.00
5.00	3.00	.	9.00
14.00	0.00	.	61.00
15.00	3.00	.	19.00
21.00	0.00	.	76.00
10.00	0.00	.	17.00
14.00	0.00	.	35.00
21.00	0.00	.	35.00

PB	ZN	AL	CR
20.00	33.00	13330.00	.
17.00	1.00	8670.00	.
17.00	17.00	7000.00	.
20.00	43.00	18500.00	.
30.00	33.00	13670.00	.
40.00	80.00	17670.00	.
0.00	67.00	11000.00	.
13.00	20.00	6670.00	.
3.00	33.00	21000.00	.

AG	MN	FE
2.00	.	.
1.00	.	.
3.00	.	.
1.00	.	.
1.00	.	.
2.00	.	.
3.00	.	.
0.00	.	.
3.00	.	.

(continued)

TABLE C-6 (continued)

SITE 2

SITECODE	ID	BA	SE	AS
20708825	BGD(30-42)	102.00	.	.
	BGD(56-62)	75.00	.	.
	2(33-37)	16.00	.	.
	2(51-60)	37.00	.	.
	4(34-40)	112.00	.	.
	4(50-54)	12.00	.	.
	6(34-38)	16.00	.	.
	6(50-58)	30.00	.	.
	2(33-37)	83.00	.	.

CU	CD	CO	NI
6.00	3.00	.	22.00
3.00	6.00	.	8.00
3.00	3.00	.	14.00
9.00	4.00	.	9.00
9.00	3.00	.	7.00
3.00	3.00	.	4.00
3.00	3.00	.	15.00
3.00	3.00	.	2.00
6.00	3.00	.	7.00

PB	ZN	AL	CR
18.00	33.00	.	18.00
7.00	16.00	.	10.00
13.00	23.00	.	13.00
9.00	28.00	.	22.00
7.00	25.00	.	19.00
6.00	15.00	.	9.00
5.00	19.00	.	16.00
7.00	4.00	.	4.00
6.00	19.00	.	16.00

AG	MN	FE
3.00	.	.
3.00	.	.
3.00	.	.
3.00	.	.
3.00	.	.
3.00	.	.
3.00	.	.
3.00	.	.
3.00	.	.

(continued)

TABLE C-6 (continued)

SITE 2

SITECODE	ID	BA	SE	AS
2122161	BGD(49-58)	.	.	.
	BGD(30-35)	102.00	.	.
	BGD(56-62)	75.00	.	.

CU	CD	CO	NI
16.00	0.00	.	39.00
6.00	3.00	.	22.00
3.00	6.00	.	8.00

PB	ZN	AL	CR
10.00	37.00	34000.00	.
18.00	33.00	.	18.00
7.00	16.00	.	10.00

AG	MN	FE
2.00	.	.
3.00	.	.
3.00	.	.

(continued)

TABLE C-6 (continued)

SITE 3

SITECODE	ID	BA	SE	AS
3122881	1(30-36)	.	.	.
	1(44-48)	.	.	.
	1(48-52)	.	.	.
	1(52-56)	.	.	.
	2(32-36)	.	.	.
	2(42-45)	.	.	.
	3(27-30)	.	.	.
	3(35-39)	.	.	.
	3(45-48)	.	.	.

CU	CD	CO	NI
2.00	0.00	.	34.00
20.00	0.00	.	22.00
60.00	0.00	.	58.00
17.00	0.00	.	49.00
37.00	0.00	.	121.00
29.00	0.00	.	55.00
62.00	0.00	.	45.00
56.00	0.00	.	42.00
50.00	0.00	.	34.00

PB	ZN	AL	CR
.	30.00	16170.00	.
.	40.00	14670.00	.
.	67.00	20830.00	.
.	93.00	23000.00	.
.	64.00	25170.00	.
.	120.00	24670.00	.
.	47.00	28000.00	.
.	50.00	20000.00	.
.	.	21670.00	.

AG	MN	FE
2.00	.	.
0.00	.	.
3.00	.	.
6.00	.	.
1.00	.	.
2.00	.	.
1.00	.	.
1.00	.	.
1.00	.	.

(continued)

TABLE C-6 (continued)

SITE 3

SITECODE	ID	BA	SE	AS
3122881	BGD(30-35)	107.00	.	.
	BGD(46-51)	64.00	.	.

	CU	CD	CG	NI
	94.00	3.00	.	9.00
	6.00	3.00	.	10.00

	PB	ZN	AL	CR
	27.00	40.00	.	18.00
	11.00	33.00	.	19.00

	AG	MN	FE
	3.00	.	.
	3.00	.	.

(continued)

TABLE C-6 (continued)

SITE 3

SITECODE	ID	BA	SE	AS
30629825	BGD(30-35)	107.00	.	.
	BGD(46-51)	64.00	.	.
	2(28-32)	39.00	.	.
	2(45-48)	53.00	.	.
	6(32-34)	61.00	.	.
	6(52-56)	75.00	.	.
	BGT	.	.	.
	BGB	.	.	0.00

CU	CD	CD	NI
94.00	3.00	.	9.00
8.00	3.00	.	10.00
6.00	3.00	.	19.00
17.00	3.00	.	37.00
44.00	3.00	.	43.00
20.00	3.00	.	25.00
15.00	0.60	7.00	40.00
8.00	0.00	13.00	16.00

PB	ZN	AL	CR
27.00	40.00	.	18.00
11.00	33.00	.	19.00
33.00	46.00	.	20.00
36.00	86.00	.	36.00
7.00	81.00	.	37.00
14.00	88.00	.	47.00
30.00	5.00	17810.00	20.00
23.00	0.00	13500.00	30.00

AG	MN	FE
3.00	.	.
3.00	.	.
3.00	.	.
3.00	.	.
4.00	.	.
3.00	.	.
4.00	0.00	.
2.00	0.00	.

Table C-7 Mean Metal Concentrations in Deep Cores at Sites

Site 1

Metal	12/30/81 (81-122 cm)	12/30/81 (127-152 cm)	6/30/81 (76-91 cm)	6/30/81 (124-140 cm)	Bkg (76-107 cm)	Bkg (142-157 cm)
Ag	4.5	3.2	3.0	4.0	<3.0	<3.0
Ba	-	-	135.3	48.5	123.0	58.0
Cd	-	-	<1.0	<1.0	<1.0	<1.0
Cr	-	-	26.3	43.0	26.0	29.0
Cu	11.5	12.5	9.0	9.0	3.0	14.0
Ni	41.6	32.8	14.3	22.0	22.0	11.0
Pb	16.5	18.3	30.3	8.0	18.0	17.0
Zn	35.0	43.8	45.5	58.0	44.0	46.0

(continued)

Table C-7 (continued)

Site 2

Metal	12/21/81 (66-91 cm)	12/21/81 (124-152 cm)	7/8/82 (84-102 cm)	7/8/82 (127-152 cm)	Bkg (76-89 cm)	Bkg (142-157 cm)
Ag	1.4	2.4	<3.0	<3.0	<3.0	<3.0
Ba	-	-	59.2	26.3	102.0	75.0
Cd	<1.0	1.5	3.0	3.3	<1.0	6.0
Cr	-	-	16.5	11.7	18.0	10.0
Cu	12.4	14.9	5.5	5.0	6.0	3.0
Ni	32.4	35.3	10.8	5.0	22.0	8.0
Pb	14.0	23.4	7.2	7.3	18.0	7.0
Zn	32.8	41.8	21.7	15.7	33.0	16.0

(continued)

Table C-7 (continued)

Site 3

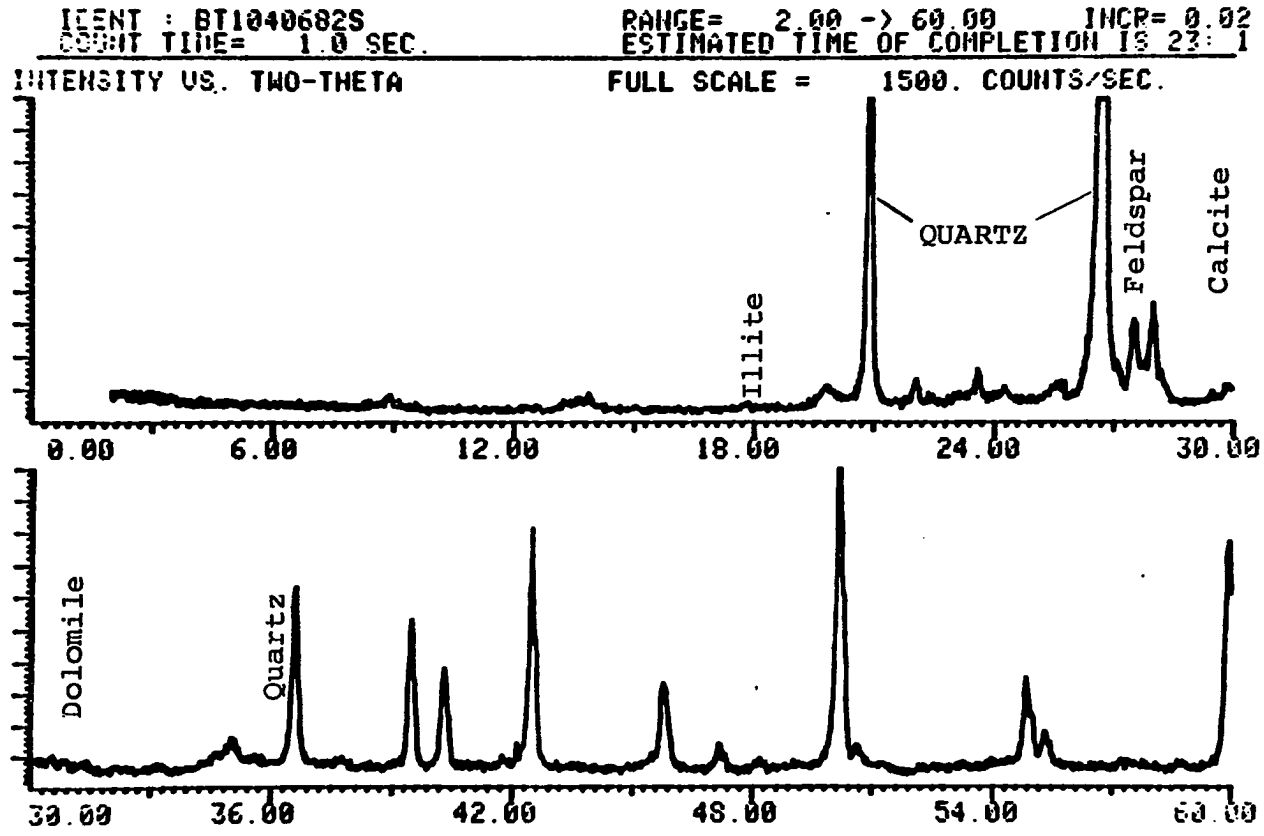
Metal	12/28/81 (71-91 cm)	12/28/81 (114-142 cm)	6/29/82 (71-86 cm)	6/29/82 (114-142 cm)	Bkg (76-89 cm)	Bkg (117-130 cm)
Ag	1.0	64.0	3.5	3.0	<3.0	<3.0
Ba	-	-	50.0	64.0	107.0	64.0
Cd	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Cr	-	-	28.5	41.5	18.0	19.0
Cu	35.4	39.0	25.0	18.5	94.0	8.0
Ni	52.8	49.0	31.0	31.0	9.0	10.0
Pb	-	-	20.0	25.0	27.0	11.0
Zn	46.2	70.0	63.5	87.0	40.0	33.0

APPENDIX D

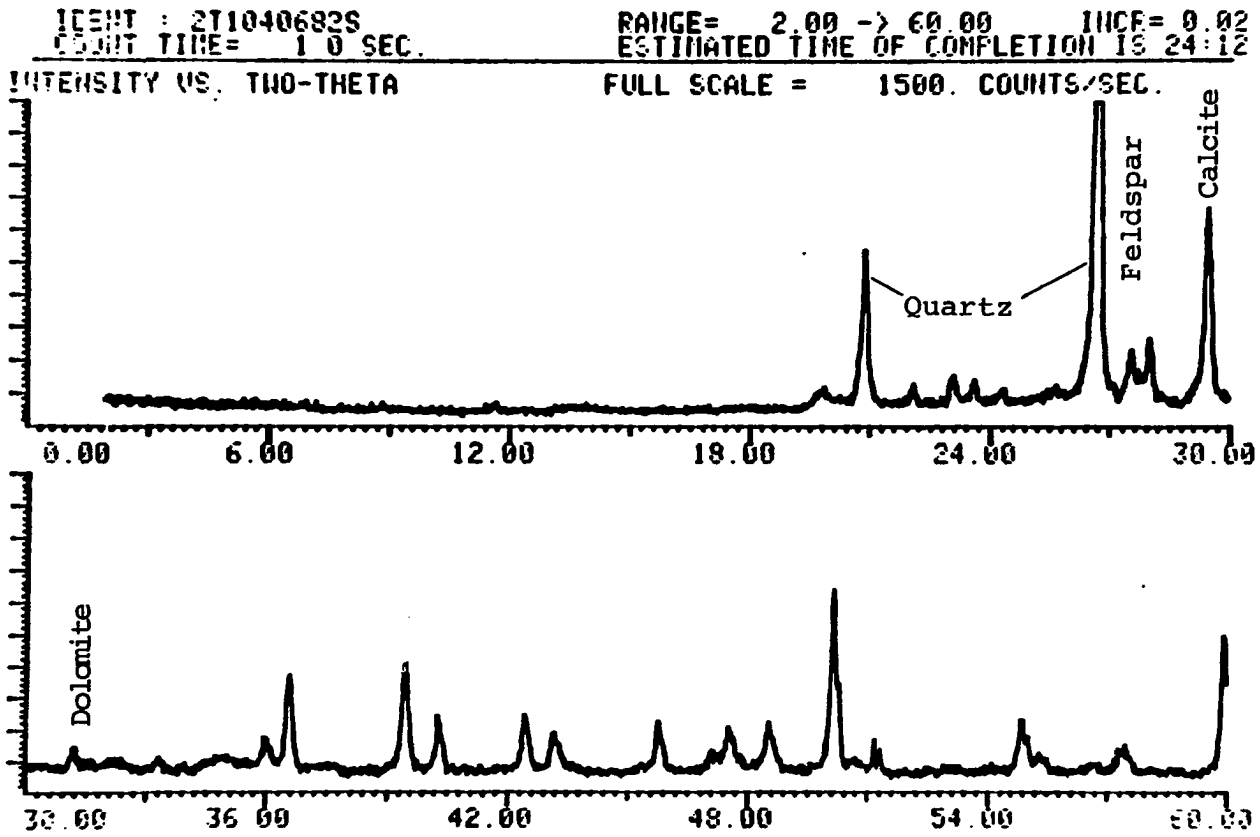
X-ray Diffraction Spectra

APPENDIX B

X-RAY DIFFRACTION SPECTRA

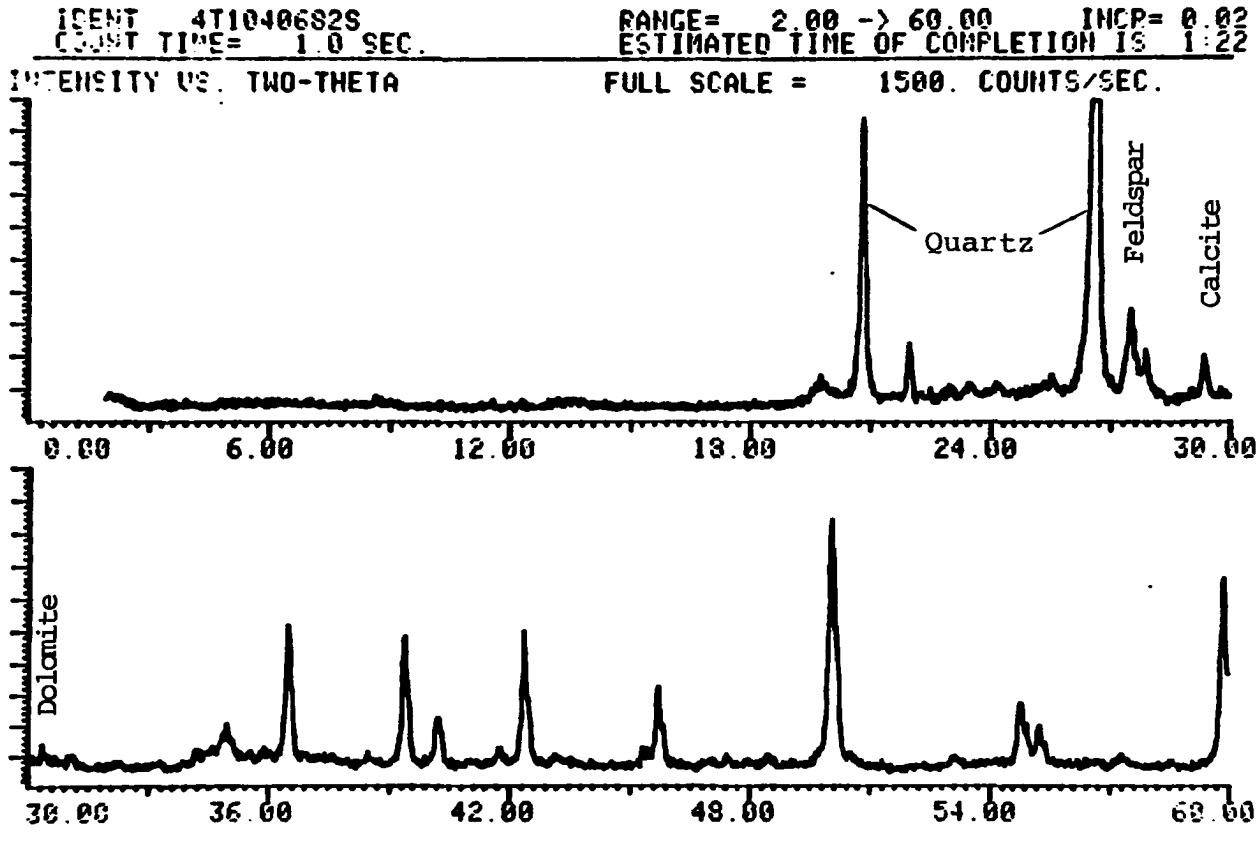


(continued) Site 1 - Background Oil Content = 0.3%

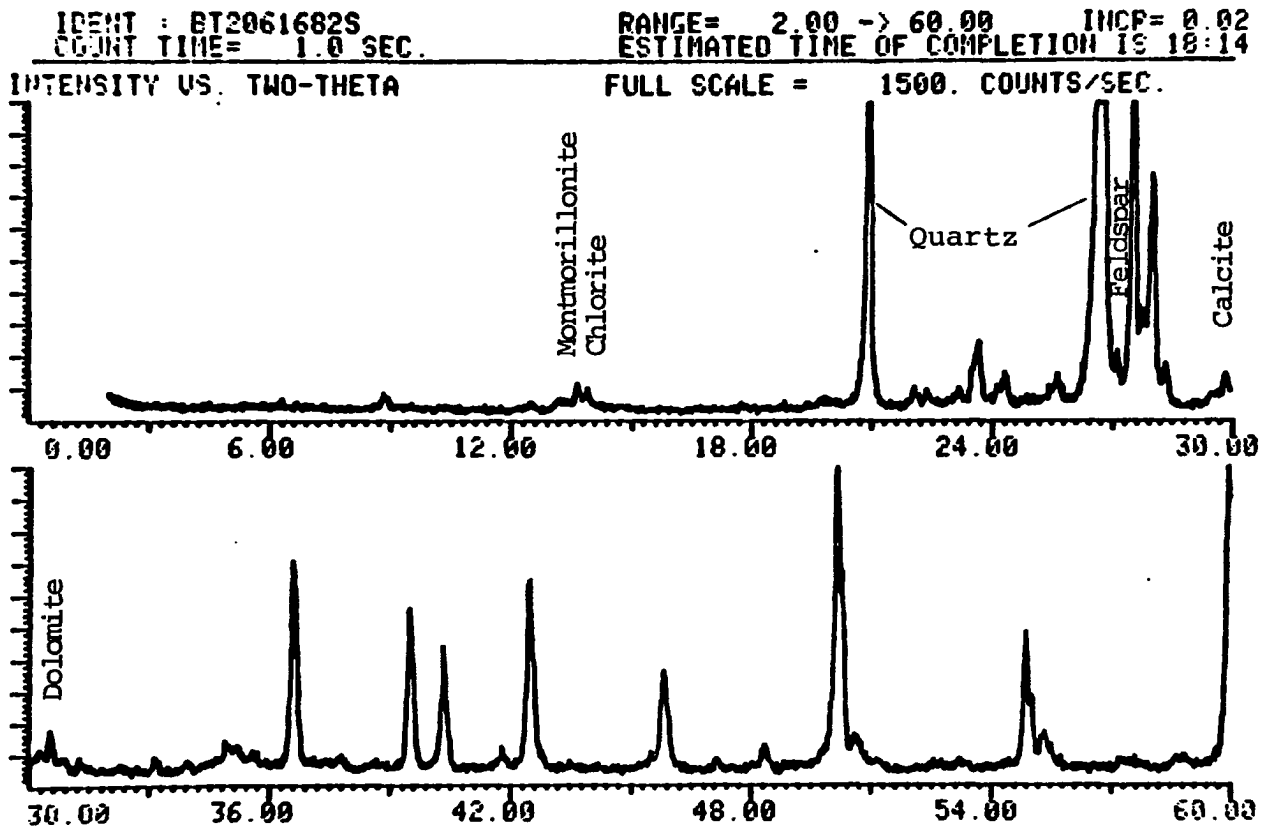


(continued) Site 1, Area 3 Top - Oil Content = 7.1%

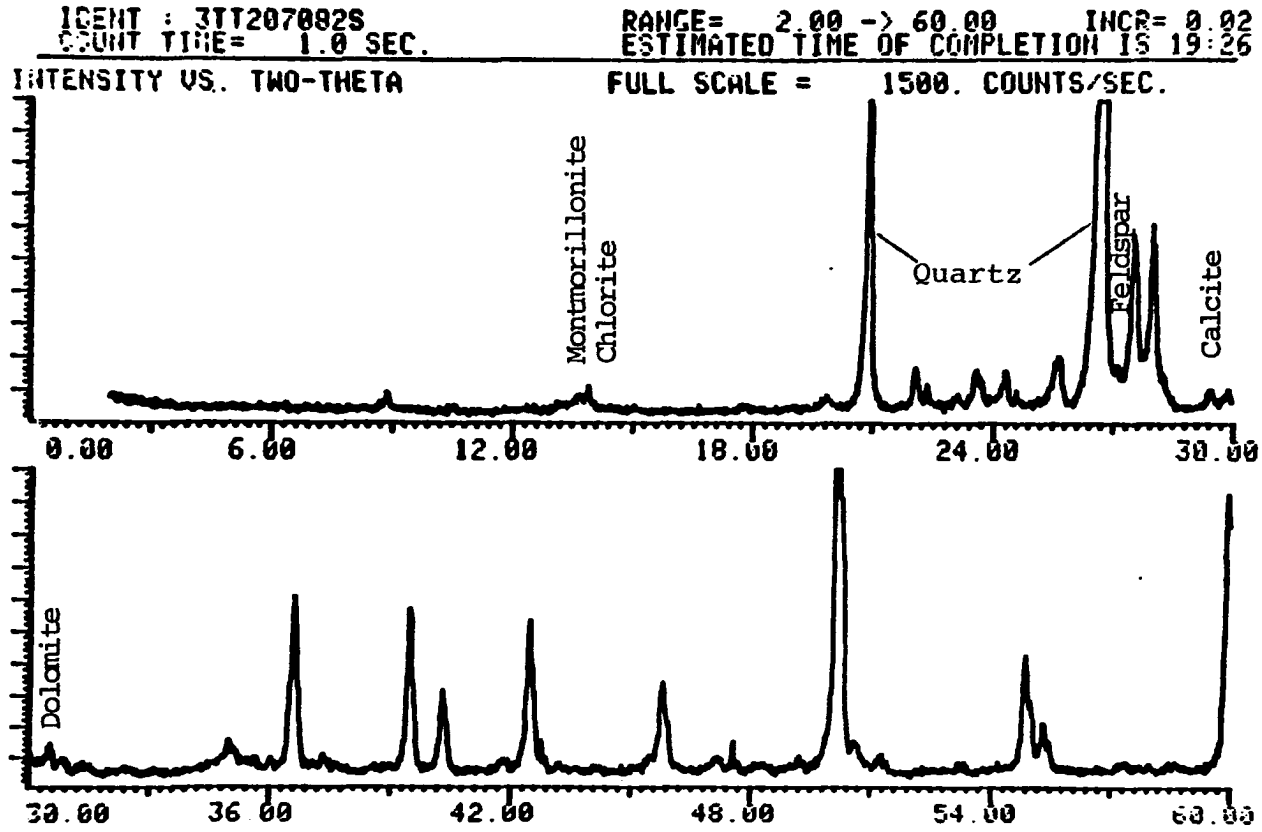
APPENDIX D (continued)



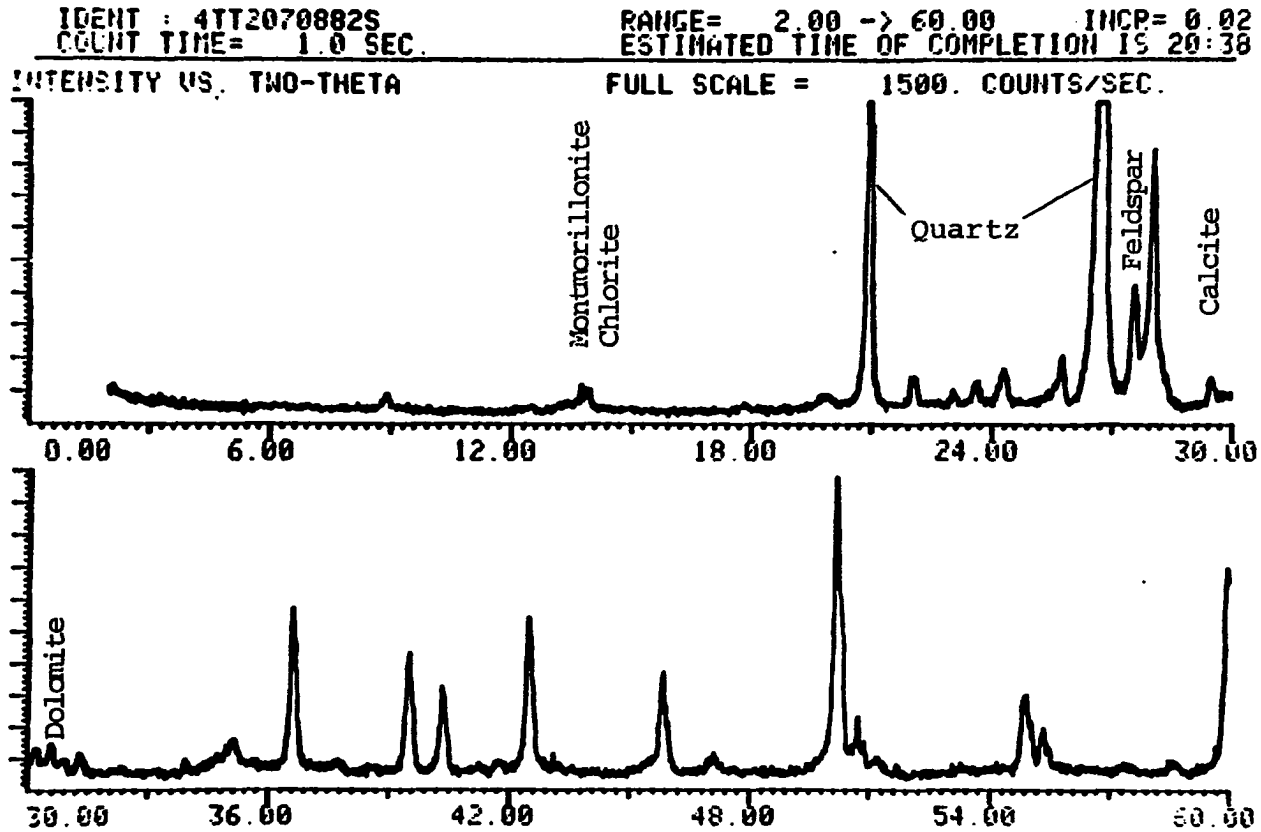
(continued) Site 1, Area 4 Oil Contents = 4.0%



(continued) Site 2 - Background Oil Content = 3.1%

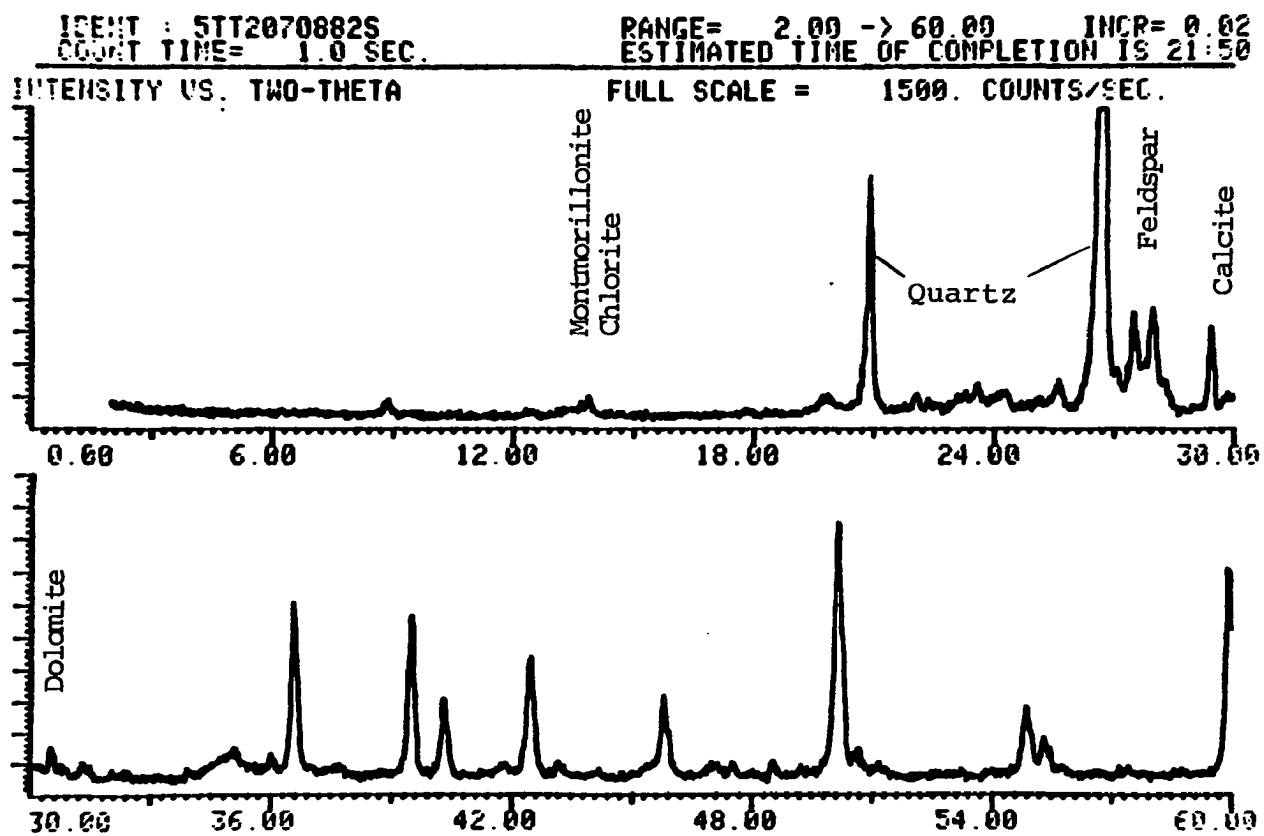


(continued) Site 2, Area 3 Oil Content = 0.5%

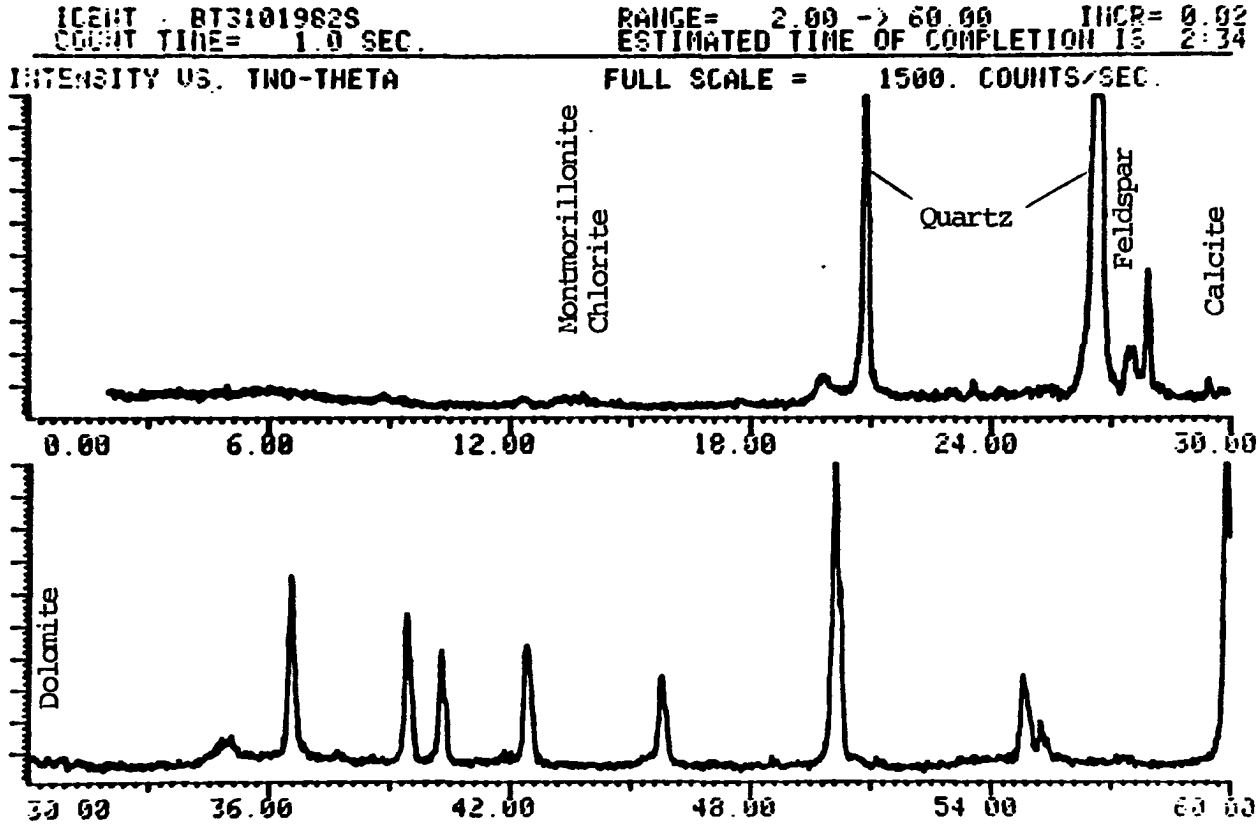


(continued) Site 2, Area 4 Oil Content = 1.8%

APPENDIX D (continued)

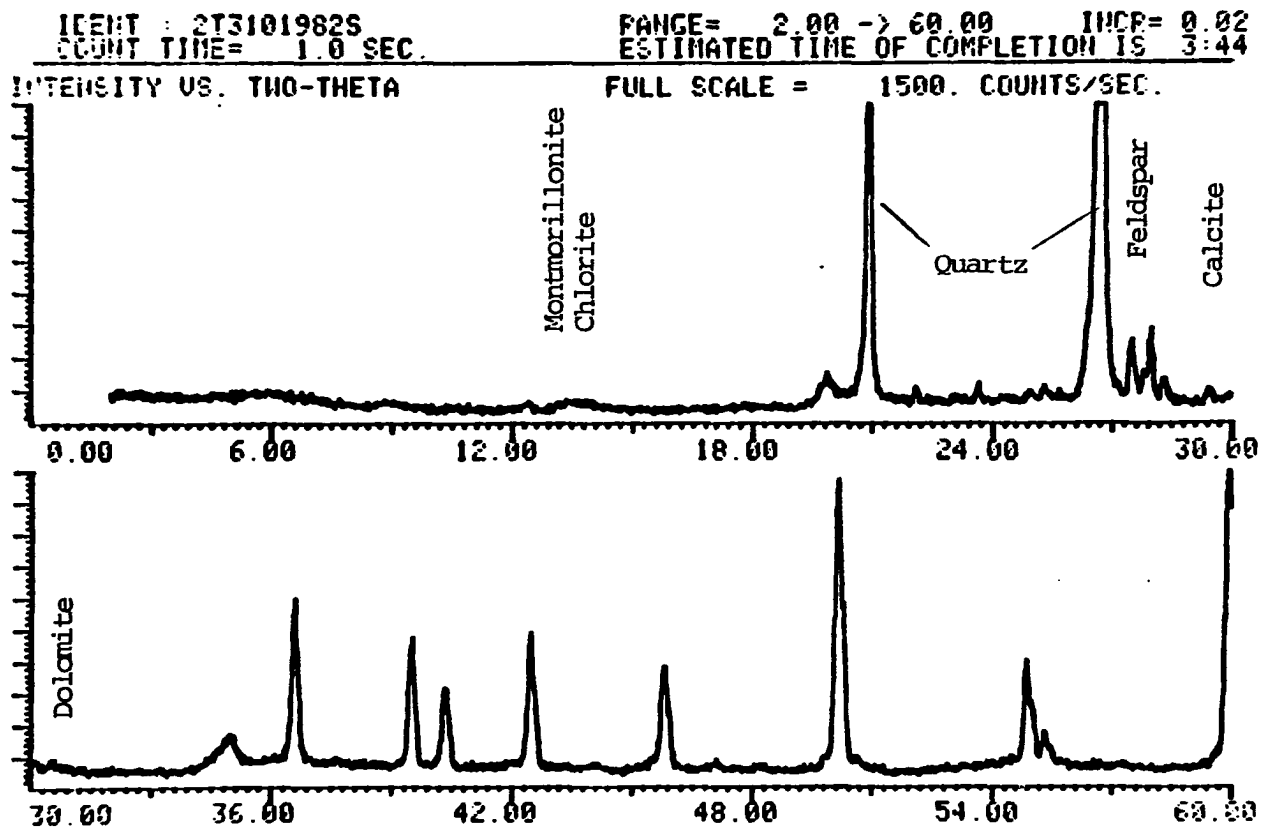


Site 2, Area 5 Oil Content = 4.0%



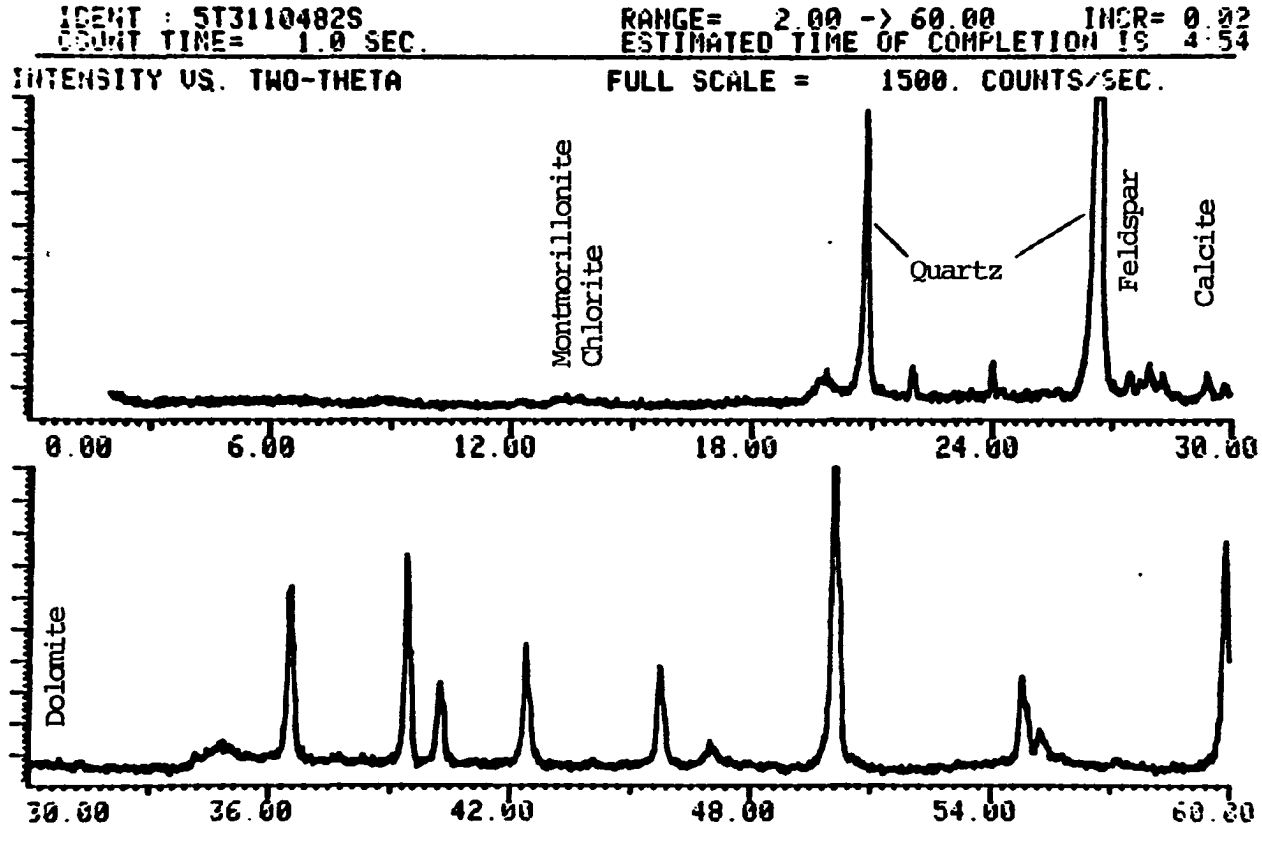
(continued) Site 3 - Background Oil Content = 0.5%

APPENDIX D (continued)



(continued) Site 3, Area 2 Oil Content = 5.2%

APPENDIX D (continued)



(continued) Site 3, Area Oil Content = 13.1%