

Effects of Oily Sludge Landfarming on the Soil Environment

by

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A Thesis Presented to the

FACULTY OF THE COLLEGE OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

CIVIL ENGINEERING

June, 1996

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Civil Engineering

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KING FAHAD UNIVERSITY OF PETROLEUM
AND MINERALS
COLLEGE OF ENGINEERING
DEPARTMENT OF CIVIL ENGINEERING

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KHALAF J. AL-ANAZI

MASTER OF ENGINEERING

JUNE 1996

KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS


Dhahran 31261, Saudi Arabia

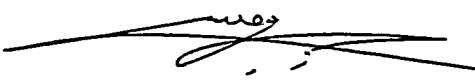
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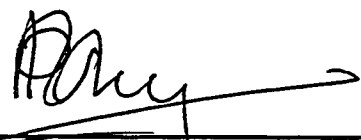
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This Master of Engineering Report written by KHALAF J. AL-ANAZI under the direction of his Advisor and approved by his Report Committee, has been presented to and accepted by the Dean of the College of Graduate Studies, in partial fulfillment of the requirements for the degree of MASTER OF ENGINEERING IN CIVIL ENGINEERING.


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ACKNOWLEDGMENT

May all praise and thanks be to ALLAH, The Almighty, with whose gracious help it was possible to accomplish this work.

I would like to thank Dr. Shaukat Farooq, the Report Advisor, for his guidance.

Also, thanks to Dr. Sahel Abduljauwad and Dr. Ashi Ashaq, Report Committee members for their valuable time.

I am very grateful to my family members for their support. Sincere thanks to my children, for many hours that should have been spent with them but were required in the preparation of the Master Degree.

ABSTRACT

Saudi Aramco has operated Ras Tanura landfarm for about 10 years to treat oily sludge. Landfarming is a managed technology which uses soil microorganisms to biodegrade oily waste. Many oil companies in the world have found that landfarming to be the safest, most cost effective and environmentally acceptable waste management technology available for the tank bottoms generated as part of its producing and refining operations.

This report is intended to explore the long term effects of the landfarming process on the soils. It is shown from the analysis of Ras Tanura landfarm data that the landfarming process did not cause any deleterious effects to the soil environment after 10 years of operation.

In addition, this report confirms the results of many laboratories researches which have shown the optimum biodegradation occurs when the oil content is at the range between 5% and 20% of the soil. At this range, the application of the sludge can be done 6 times per year at the landfarm site in Saudi Arabia.

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CHAPTER 1: INTRODUCTION

The production, transportation and storage of petroleum hydrocarbons, petroleum refining and treatment of refinery process water, all result in a considerable volume of oily water or sludge that, in turn, becomes a disposal problem. The nature of such oily sludge varies according to its origin and treatment history, but typically it consists of hydrocarbons, inorganic sediment and water. Among the disposal options for oily sludge, the "landfarming" process is attractive in its simplicity and requires a relatively low capital investment. This disposal method has been developed largely on an empirical basis.

In the last twenty five years, many controlled studies have been published on the optimization and on the overall effectiveness of landfarming (2,3,4,5,6,8).

Recently, research has moved toward the long term fate of the polynuclear aromatics (PNA) hydrocarbons fraction (9,10) in landfarms. The fact that some of the PNAs are potential carcinogens (10,11) lends special significance to the long term environmental fate of these compounds.

The other soil contaminant category is heavy metals. In Western countries, studies have concentrated on the effect of heavy metals on crops and vegetation (3). In this report, the general forms of metal in soils will be discussed. It will also discuss the sources of metal enrichment to the environment as well as background soil concentrations. The soil chemistry of each metal including solubility, metal species and soil conditions governing the

predominant form of the metal in the soil will be given. Finally, recommendations for metals loading will be given based on their accumulation in the soil.

This report will explore the long term fate of residual hydrocarbons and heavy metals during the landfarming process in Saudi Arabia. The results of this report will be very beneficial to landfarm designers and operators. The data used in this report is from a full scale landfarm at Ras Tanura Refinery.

CHAPTER 2: LITERATURE REVIEW

The first step to prepare this report was to evaluate many studies on similar topics. Other oil companies experiences also investigated to compare the result extracted from Ras Tanura landfarm. Types of oily sludge in refining and producing facilities are giving in the next chapter. These types are classified based on their sources. Also, a comprehensive literature review was performed to determined the optimum parameters that control oil biodegradation such as temperature, oxygen, moisture, pH and microbial population. The third topic which is important to this study and very well reviewed is the fate of the heavy metals in soil environment.

2.1 ACCUMULATION OF HYDROCARBONS AT USA LANDFARMS

Most full scale landfarming facilities report an increase in the oil concentration in the zone of incorporation (6"-12" top soil) over background levels. Pilot studies carried out in United States over several years indicates that most of the accumulation occurs in the first year of operation. Once the system is acclimated, a relative steady state condition has been observed where the annual oil reduction approximates the annual oil application. The oil content in the zone of incorporation at most full scale facilities ranges between 3 to 10%.

Figure 2.1 illustrates the oil content with depth for several full scale facilities at different locations in United States. The profiles are typical of refinery landfarming facilities. A wide variation in oil content is evidenced among facilities in the zone of incorporation (up to 8%) .However, the soil oil content below the zone of incorporation decreases rapidly with depth. The maximum extent of oil migration for the facilities reviewed was less than 1.5 feet below the zone of incorporation and was within the aerobic treatment zone (5' depth) of the facility.

Available data from pilot scale facilities indicate that accumulated oil will continue to degrade for several years after oil applications have terminated (i.e., the landfarm is closed). Figure 2.2 indicates that an approximately 50% reduction in soil oil concentration was observed over a two-year period at closed pilot scale facilities which had oil concentrations in the soil greater than 3% at the time of the last waste application (12). No effort was made to stimulate degradation after the last waste application at any of these plots (i.e., no cultivation or soil amendment took place).

Accumulation of oil in the zone of incorporation may impact closure activities. Available data indicate that oil concentrations above 4% may inhibit germination of annual grasses (3). If vegetation establishment is part of the closure plan, sites may require additional management (cultivation) after the last waste application to promote oil degradation.

Figure 2.1

Oil Content in Soil at US Landfarms (12)

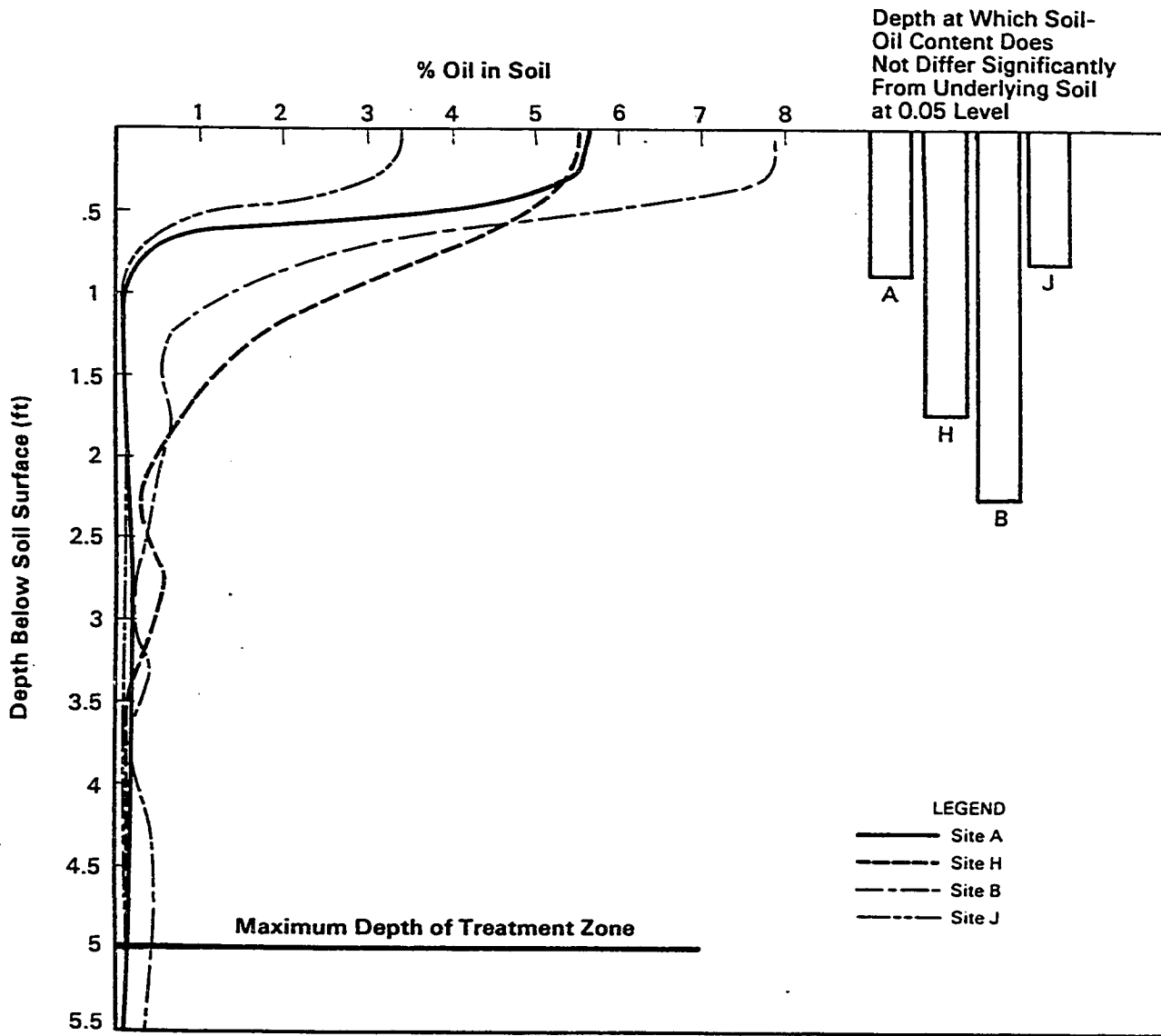
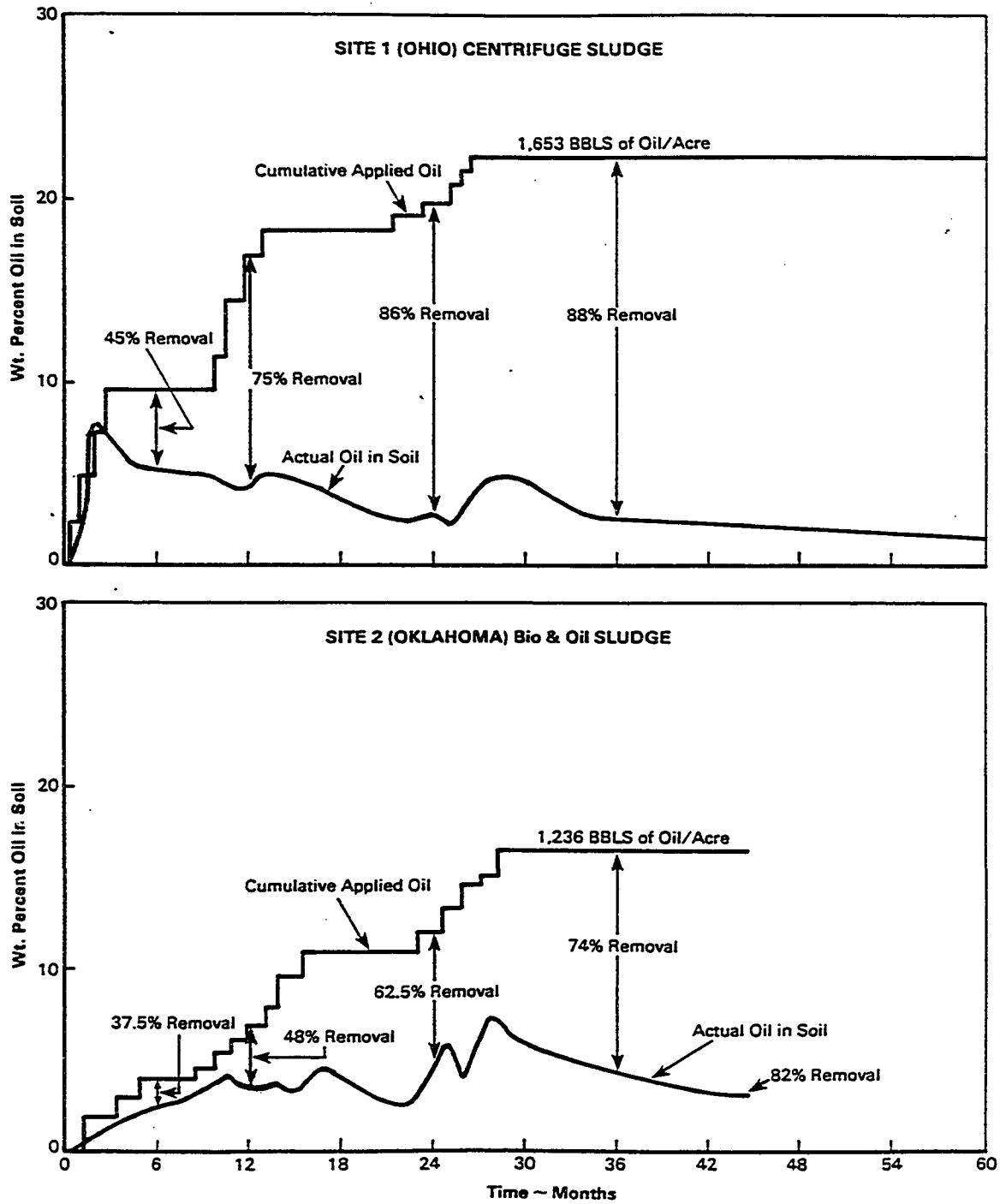


Figure 2.2

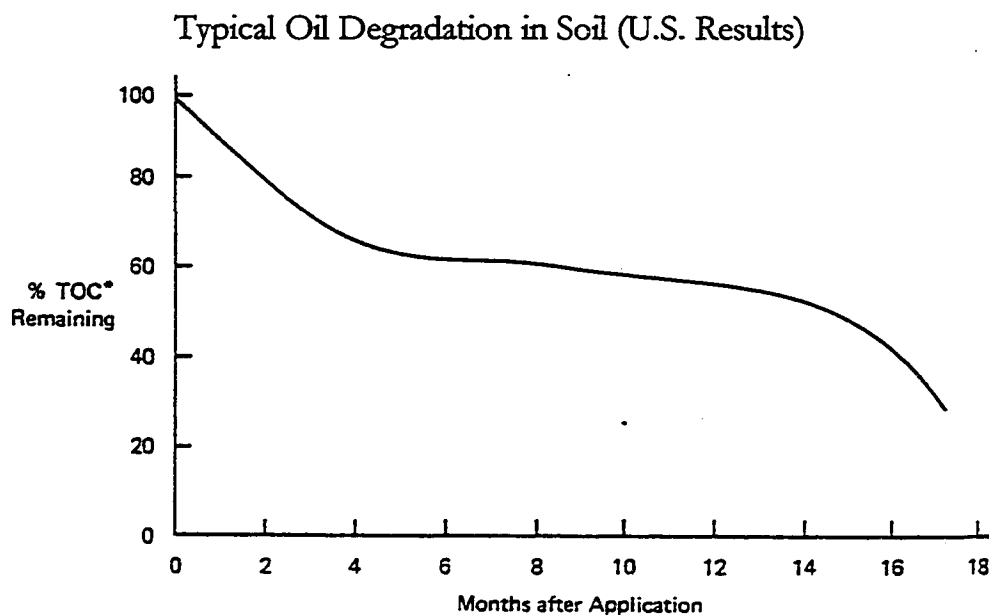
Oil Removal Rate at two Pilot Scale landfarms (12)



Evaluation of hydrocarbon fractions in the accumulated oil at land treatment facilities suggests that as the soil-oil content decreases, the concentration of heavy aromatics and asphaltenes increase in the soil. The result is that there is increase of these compounds in the soil compared to the saturated and light aromatic hydrocarbon fraction of the applied oil. A mass balance indicates however, that these compounds do degrade but at much slower rates than the overall oil reduction rate.(12)

A typical plot of the rate of degradation of oil, from some American oily sludge landfarming experiments, is given in Figure 2.3. The oil decomposition rate (represented here by Total Organic Carbon (TOC) remaining in the soil) is rapid during the first few (Summer) months, lower during subsequent (Winter) months and often increases again to a higher rate in the next growing season. This kind of relation between oil degradation and time is not expected in Saudi Arabia climate conditions since all months of the year are perfect for microbial activities.

Figure 2.3



2.2 BUILDUP OF HEAVY METALS AT USA LANDFARMS

In general, waste application at full scale landfarm has resulted in an accumulation of metals in the zone of incorporation. Table 2.1 and Table 2.2 present the mean and range of metal concentrations observed at landfarms that operated in United States and background soils near landfarming sites. Background concentrations were measured on nearby soil where wastes are applied. On-site soils are actual plots where wastes are applied. The concentrations in the surface foot of the landfarm soils are significantly higher than background values for chromium, copper, lead and zinc. All the metals are attenuated with depth, generally within 1 to 2 feet below the zone of incorporation.

The primary metals of concern in refinery wastes which are landfarmed are lead and chromium. Several refinery wastes are defined by the US Environmental Protection Agency (EPA) as hazardous waste due to the suspected presence of these metals in the wastes in elevated concentration. Figure 2.4 compares the total chromium and lead concentrations present in soil samples from four full scale facilities to the concentrations extracted using EPA Toxicity Characteristic Leaching Procedure (TCLP). The TCLP limits for defining a hazardous material are superimposed on the graphs. The TCPL concentrations extracted are several orders of magnitude less than the total metal concentrations and are not affected by the magnitude of the total concentrations within the range of concentrations and soil types evaluated.

Table 2.1

Metal Content of Active Landfarms at US

Depth Below Ground Surface (ft.)	As	Cd	Cr	Cu	Hg	Ni	Pb	V	Zn
	mg/kg Dry Soil Weight								
0-1	2.76	5.11	277	89	2.11	17.5	718	45.5	306
	0.41-16.3	0.11-10	1.5-1468	2.3-260	0.04-11	2.5-50	2.5-5560	2.5-121	7.3-1041
	15	23	30	15	23	24	30	15	22
	21	29	48	27	29	29	48	20	34
1-3	2.14	5.00	71.8	32.1	0.55	18.6	119	46	180
	0.06-11.3	0.03-10	1.4-315	2.4-75	0.01-1.8	2.9-50	1.47-1250	2.5-130	3.7-1175
	16	19	23	7	21	21	23	18	16
	36	39	49	13	41	41	49	38	22
3-5	1.89	2.15	76.3	33.7	0.42	17.0	19.5	57.3	72.6
	0.063-6.6	0.01-4	1.5-248	4.0-84	0.01-1.2	4.0-30.9	0.84-40	2.5-94.4	15.3-138
	9	14	17	8	14	13	17	13	8
	15	22	25	10	22	20	25	20	10

*Data reported as:

Average
Range
No. of Individual Plots Sampled
No. of Total Samples Collected.

Source: American Petroleum Institute, 1983.

Table 2.2

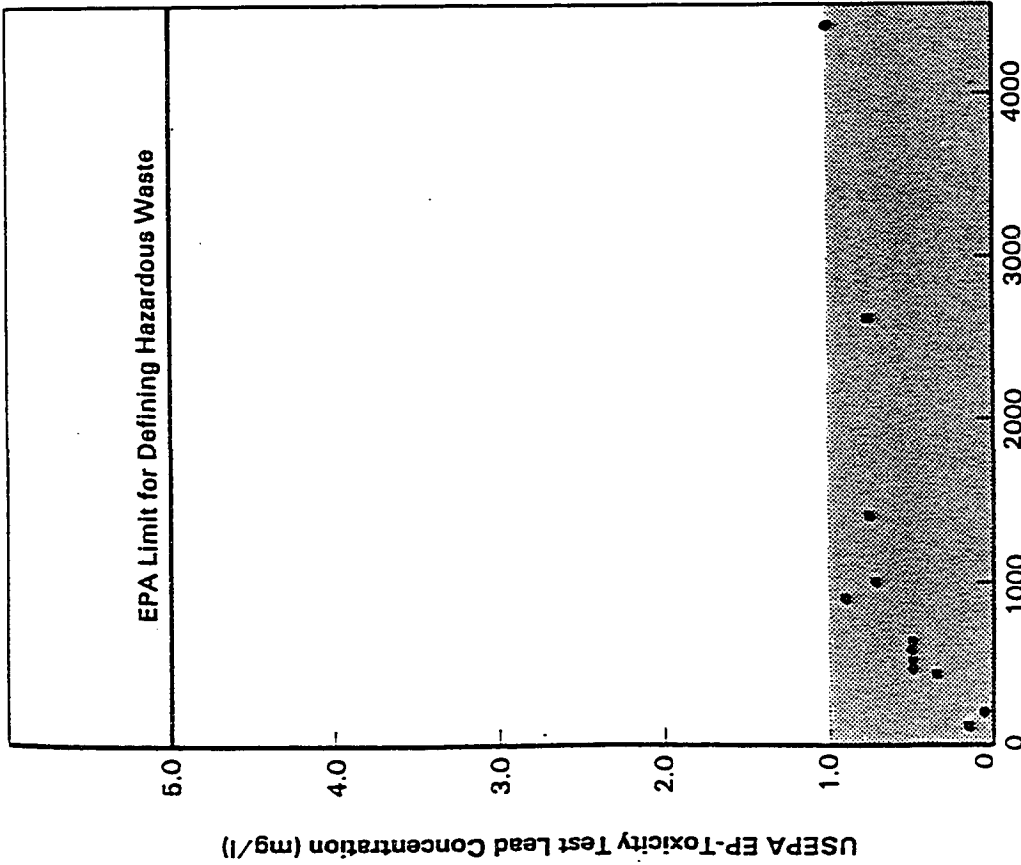
Metal Content of Background Soil Near Active Landfarms at US

Depth Below Ground Surface (ft.)	As	Cd	Cr	Cu	Hg	Ni	Pb	V	Zn
	mg/kg Dry Soil Weight								
0-1	2.74 0.08-6.2 7 16	3.51 0.07-10 9 20	65.8 1.7-244 12 23	24.3 6.3-42 5 7	0.675 0.07-1.6 9 20	17.1 1.8-50 10 18	40.5 4.91-150 12 23	52.1 2.5-109.3 9 17	92.1 16.3-156 6 9
1-3	1.79 0.1-4.8 7 27	2.42 0.03-8 7 27	30.1 2-146 9 33	8.1 7.4-8.7 2 6	0.81 0.01-1.5 8 28	15.9 4.0-36 9 28	24.5 1.1-88.5 9 33	58.6 2.5-111 9 28	74.2 9.8-176 4 9
3-5	2.37 0.11-3.9 2.07 13	1.75 0.02-4.0 7 16	37.9 2.07-152 7 16	12 - 1 3	0.74 0.01-1.4 7 16	18.7 7.9-29.0 6 13	18.7 1.26-40 7 16	84.3 44.1-152 6 13	85 - 1 3

*Data reported as:

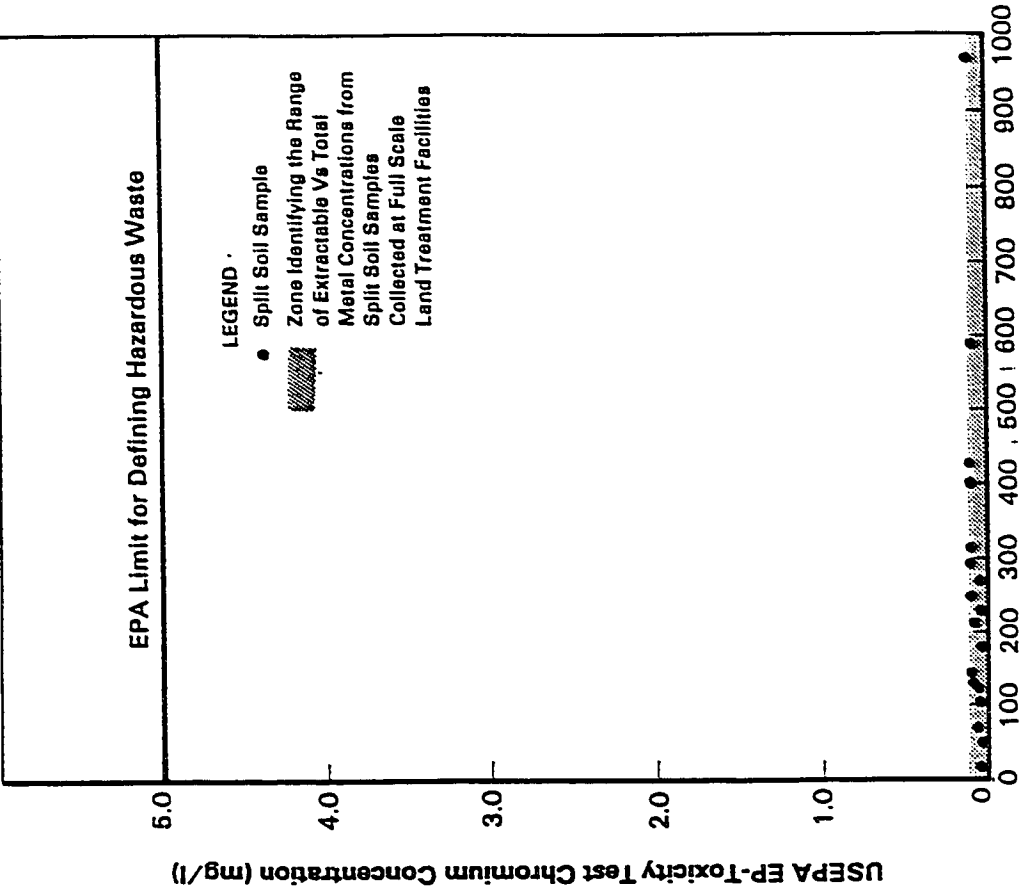
Average
Range
No. of Individual Plots Sampled
No. of Total Samples Collected.

Source: American Petroleum Institute, 1983.



Total Lead (mg/kg)
Data Developed from 12 Soil Samples
Collected at Four Full Scale Sites

Figure 2.4a Extractable Lead Concentration Vs. Total Lead Concentration for Split Soil Samples Collected from Treated Soil at Depths from 0-6 Ft. (Source: API, 1983)



Total Chromium (mg/kg)
Data Developed from 18 Soil Samples
Collected at Four Full Scale Sites

Figure 2.4b Extractable Chromium Concentration Vs. Total Chromium Concentration for Split Soil Samples Collected from Treated Soil at Depths from 0-6 Ft. (Source: API, 1983)

The TCLP test was designed to evaluate the leaching potential of wastes which are land disposed. The test involves an extraction procedure with a low pH solution to simulate soil conditions. The test is also used on waste amended soil to evaluate its leaching potential. Although this procedure exaggerates natural conditions due to the large volumes of low pH solution used, it provides a useful comparison of the relative solubility of waste constituents in the soil. Figure 2.4 clearly illustrates that lead and chromium in the soil are very insoluble even at high concentrations.

Chevron Oil Company has operated few landfarms in United States since 1970. Chevron landfarms have experienced a buildup of heavy metals on the incorporation zone soils. Table 2.3 shows the mean metals concentrations at Chevron landfarms in 1970 and 1980.(13)

Accumulation and subsequent migration of metals have been concerns at the landfarms reviewed. Several metals have been observed to exceed background values at most landfarms; however, their low solubility limits subsurface migration resulting in the immobilization of the applied metals within the treatment zone.

Table 2.3

Chevron Landfarms Mean Metal Concentrations(13)

Metal	Concentration at Chevron landfarms (ppm)	Concentration at Chevron landfarms (ppm)
	1970	1980
Cadmium	0	20
Chromium	10	150
Copper	40	500
Lead	5	400
Nickel	20	250
Vanadium	10	150
Zinc	75	1,100

2.3 PARAMETERS THAT CONTROL OIL BIODEGRADATION

The soil environment is the most complex portion of the biosphere, characterized by intimately interwoven solid, liquid and gas phases, a wide range of particle sizes and tremendous complexity in chemical composition. As compared to the very uniform marine environment, the physicochemical characteristics of various soil types differ greatly, so that the classification of soils is a broad and still evolving field of science. To determine the suitability of seawater and soils as microbial habitats and sites for hydrocarbon biodegradation, comparisons are made between certain physicochemical parameters of these environments (Table 2.4).

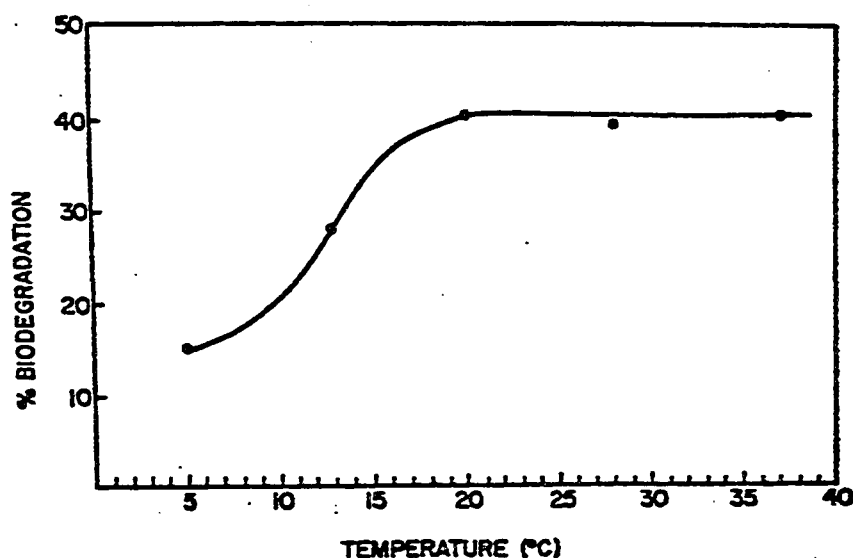
2.3.1 Temperature

Compared to seawater, in most soils conditions favorable for mesophilic prevail during at least part of the year. Psychrophiles and psychrotroph appear to find selective advantage in some polar soils. Petroleum biodegradation occurs at a wide range of soil temperatures. Freezing of the soil solution, of course, interrupts microbial activity, but a study (7) showed petroleum biodegradation at temperatures as low as -1.1°C as long as the soil solution remained liquid. Highest degradation rates, however, generally occur between $30-40^{\circ}\text{C}$. Dibble and Bartha (5) showed that the highest hydrocarbon biodegradation rates occurred above 20°C , with no further increase in rate at 37°C (Figure 2.5).

Table 2.4

Comparison of Characteristics of Oceans and Soils as Microbial Habitats (2)

Parameter	Ocean	Soil
Expanse	79% of the global surface	21% of the global surface
Temperature	-2 °C to +33 °C	-40 °C to +65 °C
pH	8.4 to 8.6	2.5 to 11
Salinity	3.4 to 3.6%	Range from 0 to salt saturation
Oxygen availability	The water is usually oxygenated but with little reserve (8 mg/l maximum)	Adequately oxygenated except when waterlogged
Inorganic nutrients	N and P are frequently limiting	N and P are frequently limiting
Organic matter	Extremely dilute, usually limiting for heterotrophic microbial activity	Relatively abundant but consisting mostly of refractory humic substances
Attachment	Absent in the water or restricted to suspended particles	Great abundance of inorganic and organic surfaces

Figure 2.5
Effect of Temperature (5)

Substrate utilization at different temperatures is often expressed in terms of Q_{10} values denoting the factor by which the rates of substrate utilization increase for each 10 °C rise in temperature. For a marine system Gibbs and Davis (6) determined an average of 2.27 for the temperature range of 6-26 °C. No similar calculations were reported for soils, but from the study done by Dibble and Bartha on oily sludge utilization in soil, a Q_{10} value of 1.7 can be calculated for the temperature range 5 to 20 °C.

2.3.2 Oxygen

The initial steps of hydrocarbon biodegradation are oxygen-dependent. Reports on an oxygen requirement for hydrocarbon biodegradation in soils support an absolute requirement for significant biodegradation activity. Oxygen depletion leads to sharply reduced hydrocarbon utilization in soil. Through parallel chromatographic and manometric measurements, researchers demonstrated that O_2 consumption of oil-amended soils, under appropriately controlled conditions, is a reliable measure of oil biodegradation. Studies on soil-derived enrichments and on oil impregnated soils consistently showed the highest rate of oil degradation when aeration was maximized.(3, 5)

The aeration status of a soil depends on the total amount of air-filled pore space, the size of the pores, the rate of oxygen consumption and the geometric distribution of the oxygen-consuming soil layer. Large amounts of air-filled pore space and large size of the pores ensure high oxygen reserves and a rapid replacement of oxygen by diffusion, respectively. Elimination of air-filled pore space, e.g., by waterlogging, reduces soil oxygen reserves to the small

amount dissolved in the soil solution. In fine textured heavy clay soils, the small size of the pores slows oxygen diffusion, and partial or complete water-saturation aggravates the situation. Large amounts of rapidly utilizable organic substrate, including hydrocarbons, tend to deplete the oxygen reserves of the soil, especially if small pore spaces or a high degree of water saturation slows oxygen replacement by diffusion. The thicker the oxygen-consuming soil layer, the slower the rate of oxygen diffusion to the deeper layers. The upper few centimeters of a hydrocarbon-contaminated soil may remain aerobic, while its deeper layers become anoxic. A high soil waste table contributes to the development of anoxic conditions in the subsoil. (3, 4)

2.3.3 Moisture

Moisture is essential to active life processes, but too much moisture in soil, as explained in the last section, interferes with the availability of oxygen. The moisture status of a soil is best expressed in terms of a percent of its moisture holding capacity. At 100% saturation, all available capillary pore spaces are filled with water. At 10% of the water holding capacity, osmotic matric forces reduce the availability of water to microorganisms to a degree that metabolic activity becomes marginal. Saturation between 50 and 80% of the water holding capacity is considered optimal for aerobic microbial activities.

Considering the above, it is somewhat surprising that the study conducted by Dibble and Bartha (5) showed no measurable difference in oily sludge biodegradation in a sandy loam within the range of 20 to 80% water saturation. At the high range, the result was probably an artifact of soil geometry. Since a very thin (2-3 mm) soil layer was used, aeration remained

adequate even at high water saturation. There is a reason to suspect that, in a field situation, oil biodegradation would be less than optimal at 80% water saturation. On the other hand, the finding that 20% water saturation is sufficient for maximal oil biodegradation appears to be valid. The partial coating of soil surface by the hydrophobic hydrocarbons reduces the waste holding capacity of the soil. Thus, more water is available for microbial metabolism in a contaminated soil than a determination prior to the oiling would indicate.

2.3.4 Soil Reaction (pH)

While the pH of the marine environment is uniform, steady, and slightly alkaline, the pH of various soils encompasses a wide range, with most of them being somewhat acidic. The marine environment is well buffered against acidification by its carbonate-bicarbonate system.

Organic or mineral acids from various metabolic processes can lower the soil pH to rather extreme values. Most bacteria have limited tolerance for acidic conditions; fungi are more resistance. Consequently, the soil pH will often determine what type of microorganisms can participate in hydrocarbon biodegradation. In addition, there is evidence that the overall rate of hydrocarbon biodegradation is higher under slightly alkaline than under acidic conditions. (2, 6)

It has been found that gas oil biodegradation in an acidic (pH 4.5) is low. Adjustment to pH 7.4 allowed a greater utilization of saturates and aromatics, but optimal biodegradation occurred only when nitrogen and

phosphorus fertilizer was also applied. Fertilization without pH adjustment did not significantly promote gas oil biodegradation. (2)

Similarly, Dibble and Bartha (5) found that hydrocarbon biodegradation was minimal in a naturally acidic soil (pH 3.7). Hydrocarbon biodegradation increased with rising soil pH in response to liming up to the higher value (pH 7.8) tested.

In general, most research has shown that soil pH strongly influences microbial activity and should be maintained between 7 and 9. The pH is easily controlled by spreading lime in soil. (2, 3, 5, 6)

2.3.5 Nutrients

In respect to heterotrophic microbial activity, the soil environment, much like the ocean, is usually limited by organic carbon. Although top soils have vastly more organic carbon per unit volume than ocean water, this organic carbon is humidified and not readily available for mineralization.

The situation in soil is obviously more complex than in the marine environment where nitrogen and phosphorus supplements consistently elicit a positive effect on oil biodegradation. The factors that appear to contribute to the varied responses in soils include the inherent nitrogen reserves of the soil, nitrogen fixation, and, last but not least, other overriding limitations such as temperature, oxygen, water, or pH that may have a more severe effect than the limitation by mineral nutrients.

The effects of mineral nutrients on the extent of biodegradation can be vary depending on the methods and quantities of applications. For example,

Hunt et al. (7) studied the effects of inorganic nutrient amendments on the biodegradation of crude oil in an acidic soil. Addition of ammonium nitrate stimulated biodegradation. However, an increase of nitrogen levels above the initial 100 ppm application actually depressed soil respiration. The authors suggested this was due to ammonia or nitrate toxicity. When the contaminated soils were amended with either NaNO_3 or NH_4Cl at a neutral pH, the stimulation of soil respiration eventually could be directly correlated to applied levels of nitrogen. There was a 4-fold increase in CO_2 evolution in samples receiving 300 ppm nitrogen.

As mentioned, available nitrogen and phosphate in the soil is essential to achieve the maximum biodegradation rate. These inorganic are easily supplied by common agricultural fertilizers. The amounts required are dependent on such factors as available nitrogen and phosphate in the waste, waste biodegradation rate, rate of waste application, and fertilizer persistence in the landfarm soil.

To estimate the initial fertilizer quantities the following can be used as a guideline: (1)

1. For readily biodegradable matter, such as certain pharmaceutical waste, 1 part of nitrogen for 25 parts of waste carbon is needed. The phosphate added should not exceed 1 to 10% of the nitrogen required.
2. For less rapidly biodegradable waste, such as oily waste, nitrogen and phosphate requirements are smaller. It is between 1 to 10% of those required for readily degradable matter. From experience Saudi

Aramco found the following ratios of carbon to nutrients provide the optimum biodegradation:

Nitrogen (Carbon - Nitrogen Ratio) 50 : 1

Phosphorous (Carbon-Phosphorous Ratio) 100 : 1

Potassium (Carbon - Potassium Ratio) 100 : 1

2.3.6 The Microbial Community of Soils

Soil vary a great deal in their suitability as microbial habitats, but discounting extreme cases such as permafrost or saline , or highly acidic soils, one may state that of all natural environments, soils are the richest microbial habitats. This generalization holds for total numbers as well as for diversity. The relative abundance of organic substrates and attachment surfaces in the soil environment are both crucial factors that favor microbial abundance and diversity. In fertile soils, viable microbial counts range between 10^7 - 10^8 per g dry soil, while direct counts are high as 10^9 per gram. The two most abundant microbial groups are bacteria (including actinomycetes) and fungi. Algae and protozoa are constrained by the lack of light penetration in relatively low numbers and diversity. (2, 4)

In fertile soil, bacterial biomass may comprise 0.015-0.5% of the soil mass; fungal biomass may reach 0.05-0.5%. Differential estimates of heterotrophic activity such as mineralization of glucose (3, 6) indicated that fungi, due to their larger biomass, are responsible for about 80% of the measured heterotrophic activity.

The most dominant bacterial genera in soils are, in descending order, *Arthrobacter*, *Pseudomonas*, *Bacillus*, *Agrobacterium*, *Alcaligenes* and *Flavobacterium*. Members of the above genera, as well as the slightly less abundant *Mycobacterium*, *Corynebacterium*, *Micrococcus* genera and various actinomycetes have been shown to have the ability to degrade at least some hydrocarbons. From the filamentous fungi, strains of the abundant genera *Aspergillus*, *Penicillium* and *Cladosporium*, and from yeasts, some strains of *Candida* and *Rhodotorula* have been implicated in hydrocarbon biodegradation.(2, 6, 8)

The highest microbial biomass, the great microbial diversity, and the abundant representation of bacterial and fungal genera capable of metabolizing hydrocarbons render soil a relatively favorable environment for petroleum biodegradation.

2.4 FATE OF HEAVY METALS IN THE SOIL ENVIRONMENT

2.4.1 General Forms of Metals in Soil

The metallic components of waste are found in a variety of forms. Metals may be solid phase insoluble precipitates, sorbed or chelated by organic matter or oxides, sorbed on exchange sites of wastes constituents or soil colloids, or in the soil solution. If an element is essentially insoluble at usual soil pH ranges (5.5-8.0) then the metal has a low concentration in the solution and cannot be absorbed by plants or leached at an appreciable rate. If the metal is weakly sorbed and soluble, then it can be transported by leaching or runoff.

Most positively charged metals remain in the treatment zone under aerated conditions where they are immobilized, either temporarily or somewhat permanently, by the properties of the soil itself. The mechanisms of metal retention by soil include chemical sorption and electrostatic bonding. Chemical sorption is a more permanent type of metal retention than electrostatic sorption and primarily due to the mineralogy of the soil. Electrostatic bonding, or ion exchange, increases as the Cation Exchange Capacity (CEC) of soil increases and is reversible. A direct comparison between CEC and sorption capacity of the soil is not possible, however, since competition between ions in the waste or present in the native soil will influence the quantity of metal ions sorbed by the soil. (4)

A variety of mathematical relationships have been used to quantify sorption of metals to soil. These models, generally called isotherms, include the linear, Freundlich, Langmuir, and various kinetic sorption isotherms. These models provide a reasonably good basis for interpolation of metal sorption.

The partitioning of metals between various chemical forms is a dynamic process, regulated by equilibrium reactions. The initial behavior of the metal after addition to the soil largely depends on its source. A complex set of chemical reactions, physical and chemical characteristics of the soil, and a number of biological processes acting within the soil govern the ultimate fate of metallic elements.(3, 4)

The total concentration of any metal, C_{total} , in a soil is equal to:

$$C_{\text{total}} = C_{\text{fixed}} + C_{\text{ads}} + C_{\text{water}} \quad (1)$$

where:

C_{fixed} = concentration of fixed metal comprising part of the structure of clay and soil minerals, in milligrams (mg) metal per kilogram (kg) soil.

C_{ads} = concentration of metal adsorbed onto the surface of soil minerals and onto organic matter exchange sites, in mg metal/kg soil.

C_{water} = concentration of metal in soil water or groundwater in equilibrium with C_{ads} , in mg soluble metal/kg soil.

C_{fixed} represents the immobile fraction of C_{total} . C_{ads} and C_{water} represent the potentially mobile fraction of C_{total} .

In general, when a dissolved element (i.e., C_{water}) is added to the soil system, it will typically convert to C_{ads} ; then convert to C_{fixed} , the relatively fixed or immobile form. Typically, at natural concentrations C_{fixed} represents at least 90% of the total concentration present in soil system. This series of reactions is illustrated as follows:



Fixation reactions are those chemical reactions, illustrated by Equation 3, that occur in soil to remove an element from migrating to water and transform (i.e., fix) the element in an unavailable or unleachable form. The element is immobilized either within the structure of a mineral or at the mineral surface. In other words, fixation attenuates a migrating element.

Adsorption is quantified in the scientific literature, utilizing the parameters from Equations 1, 2, and 3 in two ways. First, adsorption is quantified via adsorption coefficient, K_{d1} , where: (4, 11)

$$K_{d1} = C_{\text{ads}} / C_{\text{water}} \quad (4)$$

Second, adsorption is quantified via the sorption coefficient, K_{d2} , where: (4)

$$K_{d2} = (C_{\text{fixed}} + C_{\text{ads}}) / C_{\text{water}}$$

There are three important facts that should be understood concerning the parameters listed in Equation 1. (4, 11)

First, analytical data derived from the chemical analysis of the total metal content of soil (i.e., C_{total}) relays no information regarding C_{fixed} , C_{ads} , and C_{water} other than the magnitude of their combined concentrations. In other words, if a laboratory report states a soil contains 100 mg/kg total Pb, this datum cannot reveal if 1% of this concentration is potentially mobile (i.e., $C_{\text{ads}} + C_{\text{water}}$) or if 99% is potentially mobile.

At background concentrations, the relative magnitudes of the parameters listed in Equation 1 generally are:

$$C_{\text{fixed}} \gg C_{\text{ads}} > C_{\text{water}}$$

The greater part C_{total} exists as C_{fixed} and is immobile. However, this relation ranking may or may not change as C_{total} increases above the background concentration.

Second, background concentrations represent the total concentration of a metal present after soil was formed and weathered. This concentration gives no information on the loading capacity of a soil. The loading capacity can be defined as maximum amount of metal that can be added to soil which does not cause water migrating through this soil to contain a harmful concentration of that metal. In other words, knowing that a soil contains 100 mg/kg total background Pb will not reveal if soil will or will not completely convert an additional loading of 500 mg/kg into an immobile form (C_{fixed}).

Soil cleanup standards that specify the excavation or treatment of soil containing concentrations of a chemical over a background concentration are usually based on the incorrect premise that the background concentration of a chemical in soil represents a maximum concentration of a chemical which the

soil can immobilize. The background concentration only represents the total concentration present after the soil was formed and had undergone some degree of weathering; it gives no indication of the maximum concentration of a chemical which a soil can immobilize; i. e., the loading capacity of the soil.

Third, there is no “universal” analytical method or extractant which is applicable for all forms of chemicals in all soils. The test method employed is dependent upon the individual chemical to be tested, the parameter to be tested (e.g., C_{fixed} , versus C_{ads}) and the soil type. A number of established, accepted, laboratory methods exist for determining the magnitude of C_{total} , C_{fixed} , C_{ads} , and C_{water} in soil.

Typically for metals, C_{total} can be measured by wet ashing with a mixture of perchloric, nitric or sulfuric acids. For metals, C_{ads} and C_{water} can be determined using mineral acids (e.g., 0.1 N HCl), organic acids, and chelating agents (e.g., EDTA, DTPA); hot water extractions can be utilized for elements that exist as anion (e.g., B, Mo, Se).

In general, two factors primarily govern fixation reactions in a natural soil-groundwater system: soil Eh (electromotive potential) and soil pH. In general, for many elements, if Eh is low, the reduced and fixed specie should form; if Eh is high, the oxidized and more mobile specie should form. In general, the solubility of most heavy metals, including As, Cr, Pb, is inversely related to pH: the amount retained is dependent upon the pH of the soil, with retention increasing with increasing pH.

2.4.2 Heavy Metals

This section discusses the sources of metal enrichment to the environment as well as background soil concentrations. The soil chemistry of each metal including solubility, metal species and soil conditions governing the predominant form of the metal in the soil is discussed. Finally, recommendations for metal loadings are given based on accumulation in the soil.

2.4.2.1 *Cadmium (Cd)*

Cadmium is used in the production of Cd-nickel batteries, as pigments for plastics and enamels, as a fumicide, and in electroplating and metal coating. Wastes containing significant levels of Cd include paint formulating and textile wastes. The estimated mean Cd concentration of soil is 0.06 ppm, ranging from 0.01-0.7 ppm (3).

The soil chemistry of Cd is, to a great extent, controlled by pH. Under acidic conditions Cd solubility increases and very little sorption of Cd by soil colloids, hydrous oxides, and organic matter takes place.

Landfarming of Cd containing waste can affect microbial populations as well as plant and animal life. Microorganisms exhibit varying degrees of tolerance or intolerance toward Cd. Many studies have shown that 5 ppm Cd in the growing media retards Actinomycete and soil bacteria growth, but at concentrations greater than 5 ppm, the microorganisms exhibited a tolerant response and the tolerant population attained dominance in the cultures.(3, 10)

Cadmium can be quite toxic to aquatic organisms, even in concentrations of less than 1 ppm Cd in water; therefore, runoff or movement of particles containing Cd into water must be avoided. Experimental data indicate that Cd causes cancer in animals. However, there have not been any large scale epidemiological studies to show significant association between occupational exposure of Cd and cancer in workers. (3)

The U. S. National Academy of Sciences (NAS) suggests maximum cumulative applications of Cd should not exceed 3 mg/kg or 10 ppm when added in sewage sludge. U. S. EPA cumulative criteria have adjusted application levels to 5 kg/ha Cd for soils with a pH less than 6.5. For soils with pH greater than 6.5, maximum cumulative amounts of Cd are allowed to increase with the Cation Exchange Capacity (CEC) of the soil (5 meq/100 g, 5 kg/ha; 5-15 meq/100 g, 10 kg/ha; and >15 meq/100 g, 20 kg/ha). (3, 9) It is recommended that the level of Cd in wastes be reduced to below 15-20 mg Cd/kg waste by pretreatment if possible. This review indicates soil microbial populations can be affected by soil concentration of 5 ppm, but plant populations exhibit a high tolerance for the element. Therefore, the basis for Cd loading should not be phytotoxic response but the ability of the soil to immobilize Cd. Liming the soil supplies carbonates and calcium ions which help immobilize Cd. Liming also serves to maintain an equilibrium between the soluble and precipitated forms of Cd in soil, thus reducing the hazard of Cd mobilization.

2.4.2.2 Copper (Cu)

Significant amounts of Cu are produced in wastes from textile mills, cosmetics manufacturing, and sludge from hardboard production. Soil Cu content range from 2 to 100 ppm with an average around 30 ppm.(3)

The abundance of Cu enrichment to the environment has promoted studies of behavior of the element in relation to soil properties. Copper retention in soils is dependent on pH; sorption of Cu increases with increasing pH. In kaolinitic soils where clay surfaces have a net negative charge with increase pH, the amount of Cu desorbed increased as the pH was lowered from 6 to 2. The lack of adsorption of Cu at low pH may be due to competition from Mg^{2+} , Fe^{3+} , H^+ , and Al^{3+} for sorption sites. Soils selected to represent a broad range of mineral and organic contents were found to have a specific adsorption maximum at pH 5.5 of between 350 and 6000 ppm Cu in soil. Land treated Cu wastes should be limed if necessary to maintain a pH of 6.5 or greater to ensure the predominance of insoluble forms of Cu, $Cu(OH)_2$ and $Cu(OH)_3$. (3, 9)

Soil organic matter forms very stable complexes with Cu. Carboxyl and phenolic groups are important in the organic complexing of Cu in soils. Sorption of Cu to organic matter occurs at relatively high rates when the concentrations of iron and manganese oxides in the soil are low. There is some evidence that Cu bound to organic matter is not readily available to plants. Organic matter may provide nonspecific sorption sites for Cu; however, the loss of organic matter through decomposition causes a significant decrease in this retention mechanism.(3)

Clay mineralogy also plays a significant role in determining the amount of Cu sorbed. Experiments have shown that Cu^{2+} is sorbed appreciably by quartz

and even more strongly by clays. The adsorption capacity of clays increases in the order kaoninite to illite to montmorillonite. The strength of Cu sorption of soil constituents are in the following order: (3)

manganese oxides < organic matter < iron oxides < clay minerals

A column study indicated that Cu, applied as sewage sludge, with a concentration of 500 ppm did not essentially move below the zone of incorporation and that 94% of that applied was recovered from the soil. (10) This soil had a pH between 5.2 and 6.7 and a CEC of 4.4 to 9.7 meq/100 g. Soil components which are less significant in Cu attenuation include free phosphates, iron salts, and clay-size aluminosilicate minerals.

Cation exchange capacity is a soil property indirectly related to mineralogy which may influence metal loading. It has been suggested that loading rates based on CEC only be used as a suggestion of buffering capacity of the soil and critical cumulative limits for Cu have been adjusted to soil CEC (0-5 meq/100 g, 125 kg/ha; 5-15 meq/100 g, 250 kg/ha; 15 meq/100 g, 500 kg/ha). (3)

Copper is essential to the metabolic processes common to decomposing bacteria, plants and animals. Small quantities of Cu activated enzymes required in respiration, redox-type reactions and protein synthesis. Copper has been shown to be magnified within the food chain and moderate levels of Cu ingested by ruminants may be poisonous unless the effects are alleviated through proper diet supplements of molybdenum or sulfate. The NAS recommends a soil accumulation of 250 ppm Cu in the upper 15 cm of soil. (3)

2.4.2.3 Chromium (Cr)

The sources of Cr in waste streams are from its use as a corrosion inhibitor and from dyeing and tanning industries. Chromium is used in the manufacture of refractory bricks to line metallurgical furnaces, chrome steels and alloys, and in plating operations. Other uses of Cr include topical antiseptics and astringents, defoliants for certain crops and photographic emulsions. Chromium is widely distributed in soil, water, and biological materials. The range of Cr in native soils is 1-1000 ppm with an average concentration of 100 pp. Soils derived from serpentine rocks are very high in Cr. (3)

The Cr in most industrial wastes is present in the +6 oxidation state as chromate (CrO_4^{-2}) or as dichromate ($\text{Cr}_2\text{O}_7^{-2}$). In this +6 or hexavalent form, Cr is toxic and quite mobile in soil. Under acid conditions there is a conversion from chromate to dichromate. Soluble salts of Cr, such as sulfate and nitrate, are more toxic than insoluble salts of Cr such as oxides and phosphates. This toxicity becomes more important as the acidity of the soil is increased.

Downward transport of Cr will be more rapid in coarse-textured soils than in fine textured soils because of the larger pores, less clay and faster downward movement of water. Chromium (III) readily precipitates with carbonates, hydroxides, and sulfides, and would likely be a means of reducing leaching (3, 9). These precipitation reactions are also favored by a $\text{pH} > 6$.

Chromium has been shown to be toxic to plants and animals, and recent studies indicate it may also be toxic to soil microorganisms. It was found that levels as low as 7.5 ppm in the growth media were toxic to gram negative bacteria including *Pseudomonas* and *Nocardia*. This indicate that soil microbial

transformations such as nitrification and hydrocarbon degradation may be adversely affected by Cr. The NAS recommends a soil accumulation of 1000 ppm Cr in the upper 15 cm of soil. (3)

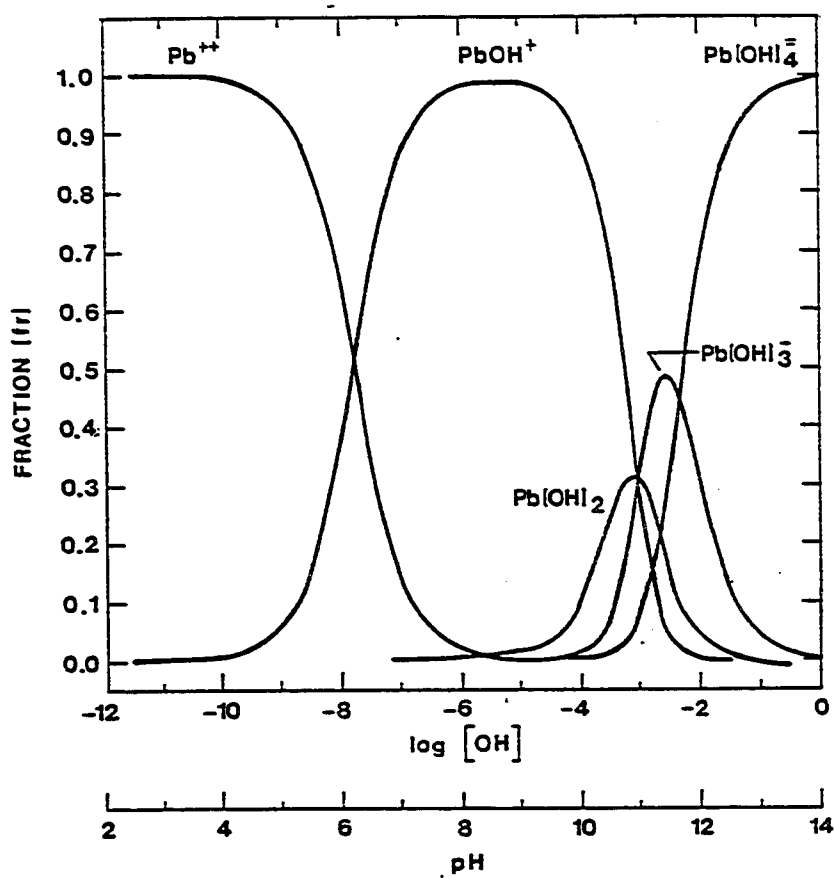
2.4.2.4 Lead (Pb)

The primary source of Pb in hazardous waste is from the manufacture of Pb-acid storage batteries and gasoline additives (tetraethyl Pb). Lead is also used in the manufacture of ammunition, caulking compounds, solders, pigments, paints, herbicides and insecticides. The Pb content of sewage sludge averages 0.17%. In coal, Pb content may range from 2-20 ppm. (3)

A Pb concentration of about 10 ppm is average for surface soils. Some soil types, however, can have a much higher concentration. In soils derived from quartz mica schist, the Pb content may be 80 ppm. The concentration in soil derived from black shale may reach 200 ppm Pb.

Lead is present in soils as Pb^{2+} which may precipitate as Pb sulfates, hydroxide and carbonates. Figure 2.6 illustrates the various Pb compounds present according to soil pH. Below pH 6, $PbSO_4$ (anglesite) is dominant. $PbCO_3$ is most stable at pH values above 7. The hydroxide $Pb(OH)_2$ controls solubility around pH 8, and lead phosphates, of which there are many forms, may control Pb^{2+} solubility at intermediate pH value. Solubility studies with molybdenum (Mo) show that $PbMoO_4$ is a reaction product and will govern Mo concentrations in soil solution.

Figure 2.6
Distribution of molecular and ionic species of
divalent lead at different pH values (2)



The availability of Pb in soils is related to moisture content, soil pH, organic matter, and the concentration of calcium and phosphates. Under waterlogged conditions, naturally occurring Pb becomes reduced and mobile. Organometallic complexes may be formed with organic matter and these soil organic chelates are of low solubility. Increasing pH and calcium (Ca^{2+}) ions diminish the capacity of plants to absorb Pb, as Ca^{2+} ions compete with the Pb^{2+} for exchange sites on the soil and root surfaces.

The Pb adsorption capacity of Illinois soils has been found to reach several thousand kilograms per hectare (3). In another study, only 3 ppm soluble Pb was found three days after 6,720 kg Pb/ha was added to the soil (5). Lead is adsorbed most strongly from aqueous solutions by calcium bentonite.

The use of irrigation water that contains the upper limit of the acceptable concentration of Pb as recommended by the National Academy of Sciences (NAS) is equivalent to an accumulation of 1,000 ppm of lead in the upper 15 cm of the soil. If demonstration of treatability experiments verify immobilization of Pb at high concentration, 1,000 ppm total Pb could be safely allowed to accumulate in soil.

2.4.2.5 Nickel (Ni)

The primary uses of Ni are for production of stainless steel alloys and electroplating. It is also used in the production of storage batteries, magnets, electrical contacts, spark plugs and machinery. Compounds of Ni are used as pigments in paints, cellulose compounds and cosmetics.

The average Ni content in the earth's crust is 100 ppm. In soil, the typical range of Ni is 5-500 ppm. Soil derived from serpentine may contain as much as 5,000 ppm Ni. (3, 9)

Nickel in soil associates with O^{2-} and OH^- ligands and is precipitated as Ni hydroxyoxides at alkaline pH. In an aerobic systems, Ni may be reduced to lower oxidation states. Nickel present in the lower oxidation state tends to precipitate as Ni carbonate and Ni sulfide.

The effects on nitrification and carbon mineralization by adding 10-1000 ppm Ni to a sandy soil were studied (3). It was found that high levels of the element may decrease both processes by 35% to 68%. These results may imply that high Ni concentrations in an organic waste may inhibit the decomposition of the waste by reducing these processes.

The use of irrigation water that contains the upper limit of the acceptable concentration of Ni as recommended by NAS is equivalent to an accumulation of 100 ppm of Ni in the upper 15 cm of soil. (3)

2.4.2.6 Zinc (Zn)

Zinc wastes originate primarily from the production of brass and bronze alloys and the production of galvanized metals for pipes, utensils and building. Other products containing Zn include insecticides, fungicides, glues, rubber, inks and glass.

Surface soils generally contain between 10-300 ppm Zn, with 50 ppm being the average value. Zinc in soil can exist as a precipitated salt, it can be adsorbed

on exchange sites of clay or organic colloids, or it can be incorporated into the crystalline clay lattice. Zinc can be fixed in clay minerals by isomorphic substitution where Zn^{2+} replaces aluminum (Al^{3+}), iron (Fe^{2+}) or magnesium (Mg^{2+}) in the octahedral layer of clay minerals. Zinc substitution also occurs in ferromagnesium minerals, augite, hornblends and biotite. Zinc bound in these minerals composes the majority of Zn found in many soils. (3, 9)

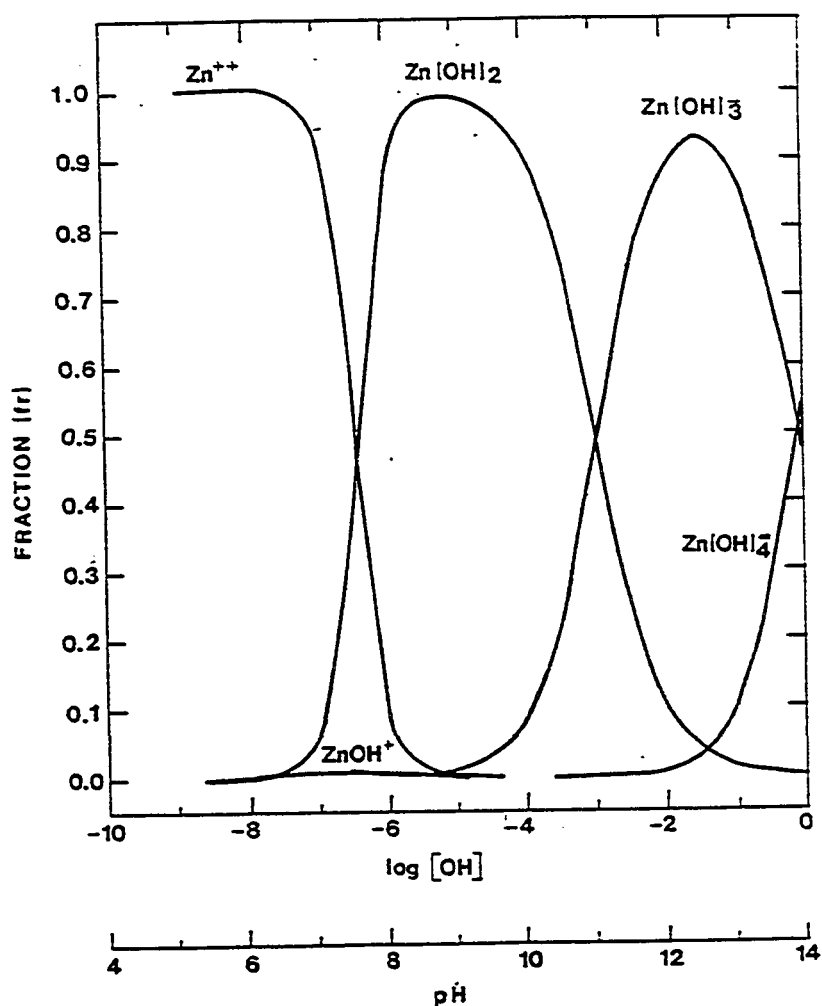
Zinc found on the exchange sites of clay minerals may be absorbed as Zn^{2+} , $\text{Zn}(\text{OH})^+$, or ZnCl^+ . The intensity of this adsorption is increased at elevated pH. It appears that potassium competes with Zn for the clay mineral exchange sites.

When Zn is complexed with chlorides, phosphates, nitrates, sulfates, carbonates and silicates at higher Zn concentrations, soluble precipitates are slowly formed. The relative abundance of these precipitates is governed by pH. On the other hand, the zinc salts, sphalerite (ZnFeS), zincates (ZnO), and smithsonite (ZnCO_3) are highly soluble and will not persist in soils for any length of time. Zinc sulfate, which is formed under reducing conditions, is relatively when compared to other zinc salts. (3)

The predominant Zn species in solutions with a pH less than 7.7 is Zn^{2+} , while ZnOH^+ predominates at a pH greater than 7.7. Figure 2.7 illustrates the forms of Zn that occur at various pH values. The relatively insoluble $\text{Zn}(\text{OH})_4^{2-}$ predominate at a soil pH between 9 and 11, whereas $\text{Zn}(\text{OH})_3^-$ and $\text{Zn}(\text{OH})_4^{2-}$ predominate at a soil pH greater than 11. The complexes, ZnSO_4 and $\text{Zn}(\text{OH})_2$, control equilibrium Zn concentrations in soil at a low pH and high pH, respectively.(3)

If proper precautions are used, Zn additions to soils need not pose environmental problems since Zn is rendered insoluble in soils where the pH values are maintained above 6.5.

Figure 2.7
Distribution of molecular and ionic species of
divalent zinc at different pH values (2)



2.4.2.7 Vanadium (V)

The major industrial uses of Vanadium are steels and nonferrous alloys. Compounds of Vanadium are also used as industrial catalysts, driers in paints, developers in photography, mordants in textiles, and in the production of glasses and ceramics.

Vanadium is widely distributed in nature. The average content in the earth's crust is 250 ppm. Soils contain 20-500 ppm V with an average concentration of 100 ppm. (3, 9)

In soils, Vanadium can be incorporated into clay minerals and is associated with aluminum (Al) oxides. Vanadium in soils may be present as a divalent cation or an oxidized anion. Vanadium may be bound to soil organic matter or organic constituents of waste and also bound to Al and iron oxide coating on organic molecules.

CHAPTER 3: OBJECTIVES

The main objectives of this study are as follows:

1. To determine the impacts of the oily sludge landfarming on the soil. Specifically, determine the accumulation of hydrocarbons and buildup of heavy metals in the landfarm soil.
2. To determine the maximum application frequency at landfarm in Saudi Arabia.

In order to determine the effects of landfarming on the soil, historical data about the landfarm operation and monitoring were needed. Data of about 10 years old were required to accomplish this study. Stacks of files were inspected to locate related information. Many people were interviewed to clarify laboratories results such as the analytical methods. These data were scattered between Ras Tanura, Dhahran and Abqiaq. It required an extensive efforts and long time to find the necessary information to prepare this report.

In addition, a full description of the remediation activities which had been performed at Ras Tanura landfarm before the closure have been given in this report. The remediation activities were carried out at the site for six months to insure that the hydrocarbons content drops below 3% before any construction can take place at the site. The results of the remediation activities have assisted on determining the biodegradation rate at this part of Saudi Arabia.

CHAPTER 4: METHODOLOGY

4.1 HISTORY OF RAS TANURA LANDFARM

Saudi Aramco began its experience with landfarming in 1982 by constructing a pilot landfarm area (Figure 4.1) at Ras Tanura Refinery. The conclusions reached as a result of this pilot landfarm were: (1)

1. Disposal of refinery sludge, which is primarily tank bottoms, by landfarming is possible.
2. Physical observations of saturation of the soil indicated that an initial soil loading of 950,000 liters per hectare is possible with subsequent loading of 475,000 liters per hectare per month.
3. Sludge application must be rigidly controlled to avoid excessive site loading and the disposal of unauthorized wastes such as tetraethyl lead contaminated sludge.

Based on the experience gained from the pilot landfarm, Saudi Aramco established a permanent 7 hectare landfarm facility during the last quarter of 1983 which included the original pilot landfarm site. Site vegetation was removed; the site was separated into several sections; an elevated roadway/dike was constructed around the facility to control surface runoff and permit site access; and pipe barricades with gates were installed around the perimeter to maintain control over sludge disposal (Figure 4.1).

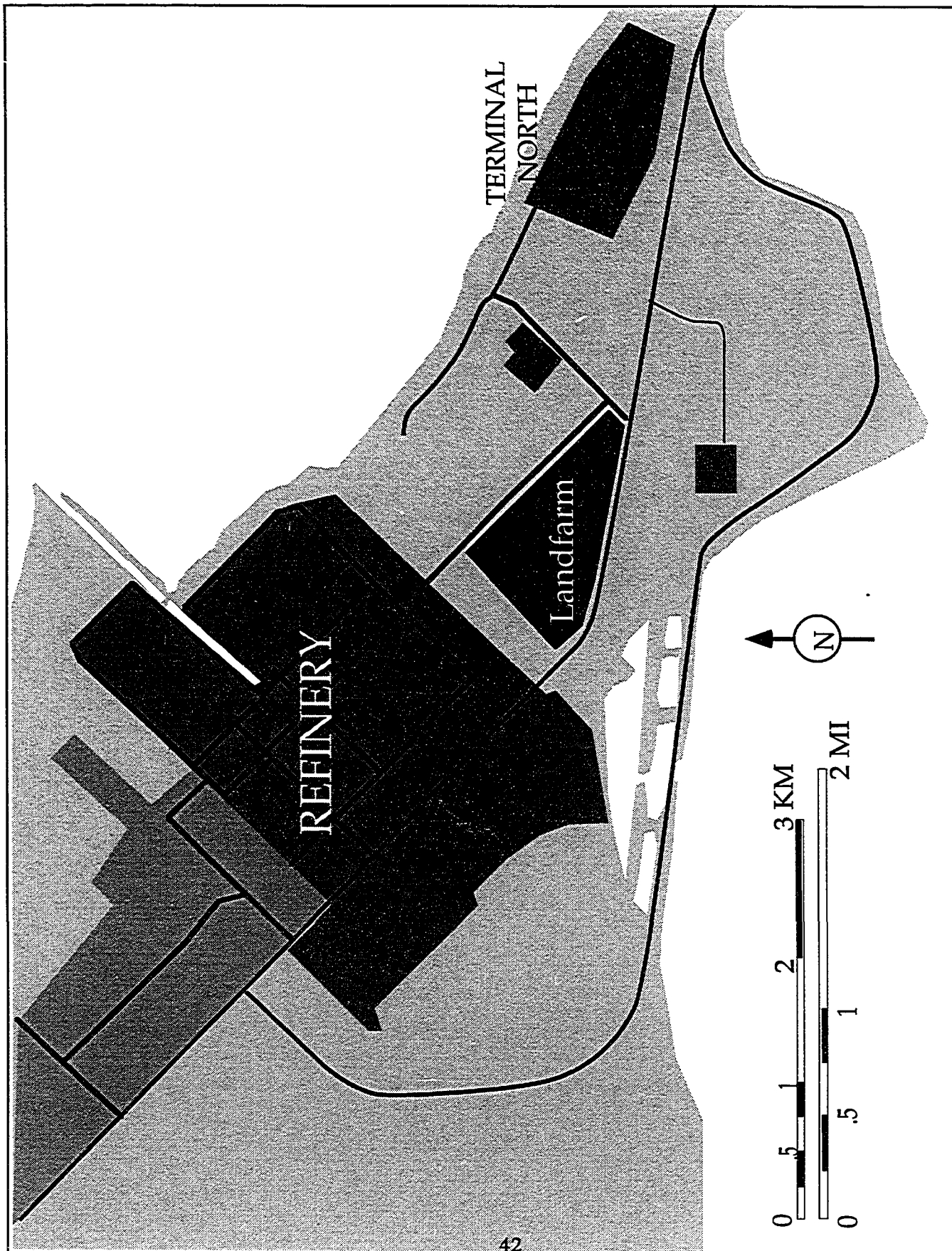


Figure 4.1: Ras Tanura Landfarm

In October, 1984, the first sludge application was made. Approximately 230,000 liters of sludge and 150,000 liters of wash water originating from the cleaning of an API separator were disposed in half of Section A. This material was transported to the landfarm site, deposited in a thick layer, and evenly spread by a bulldozer. The site was cultivated frequently by using a tractor with a disc harrow.

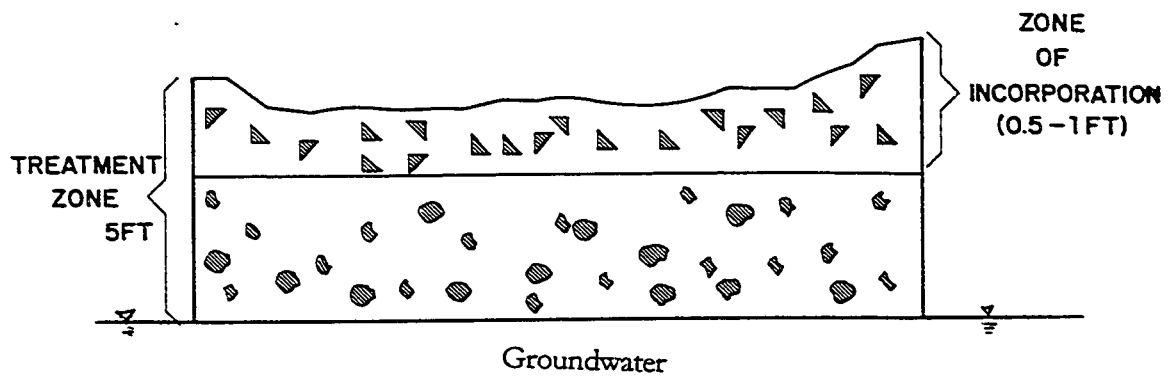
Saudi Aramco operated this landfarm continuously until December, 1993, when the company decided to close the landfarm due to the necessity of the site for the Refinery Upgrade Project.

4.2 METHODOLOGY OF THE STUDY

4.2.1 Site Selection

The Ras Tanura landfarm site was selected for its accessibility by the refinery personnel. The site is located within the refinery fenced area. The site soil is cultivable and the ground surface is flat. There were vegetation which was a good indication of presence of the required microbial population. In addition the groundwater table is at 5 ft depth from the surface which is enough depth to prevent groundwater contamination when the site properly operated. Figure 4.2 shows cross-sectional view of Ras Tanura landfarm.

Figure 4.2
Ras Tanura landfarm- cross-section view



4.2.2 Oily Waste Loading

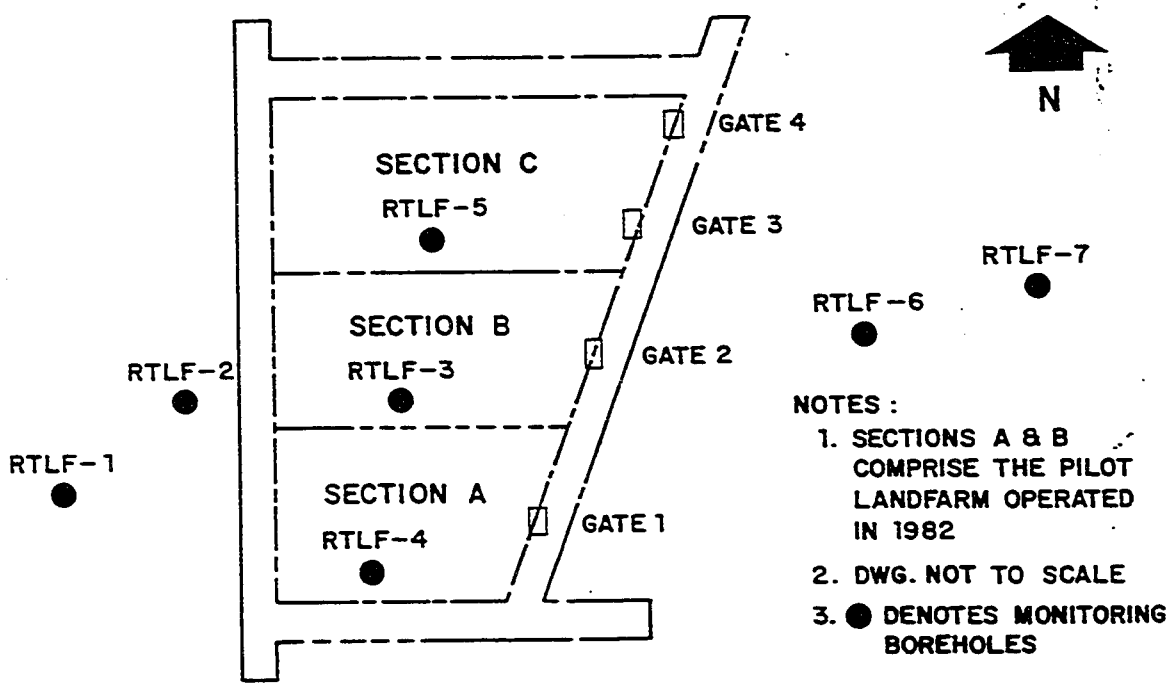
As mentioned earlier that Saudi Aramco started an initial loading of 475,000 liter per hectare per month (47.5 liter per square meter per month). Later Saudi Aramco develops a general rule on proper application of sludge. When the site is used for the first time, the initial load should be 15 liters of oil per application per square meter of land area (100 bbl per acre). Subsequent applications may be increased by an increment of 7.5 liters per square meter depending on incorporation of the waste in the soil and degradation rate. Waste application rates shall be set at levels not to exceed 50 liters of oil per application per square meter. The maximum annual waste application shall not exceed 225 liters of oil per square meter. Reapplication may occur when the soil oil content is less than 5%. These guideline were followed during the operation of Ras Tanura landfarm since 1990. Saudi Aramco is strictly following these rules in other new landfarms.

4.2.3 Monitoring Wells

When Saudi Aramco established Ras Tanura landfarm, 7 monitoring well were drilled to make sure that the landfarm operations will not contaminate the groundwater. Two of these wells were drilled up gradient and two of them were drilled down gradient. The other three were drilled at different sections of the landfarm. These wells are intended to monitor groundwater quality at these sections. Figure 4.3 shows the locations of these wells the landfarm. Background samples were collected from these wells and analyzed prior to

application of the sludge.

Figure 4.3
Monitoring Wells Locations



4.2.4 Cultivation

The most important aspect of landfarm operation is cultivation. The purpose of cultivation are to (a) break up the sludge crust (which will have formed as a result of water evaporation and percolation) and intimately mix it with the top soil, and (b) enhance soil aeration. The net effect is to speed up the rate of hydrocarbon decomposition.

The first cultivation usually conducted after 2 days of sludge application. Frequencies of once per week is required by Saudi Aramco landfarms Operation Plan.

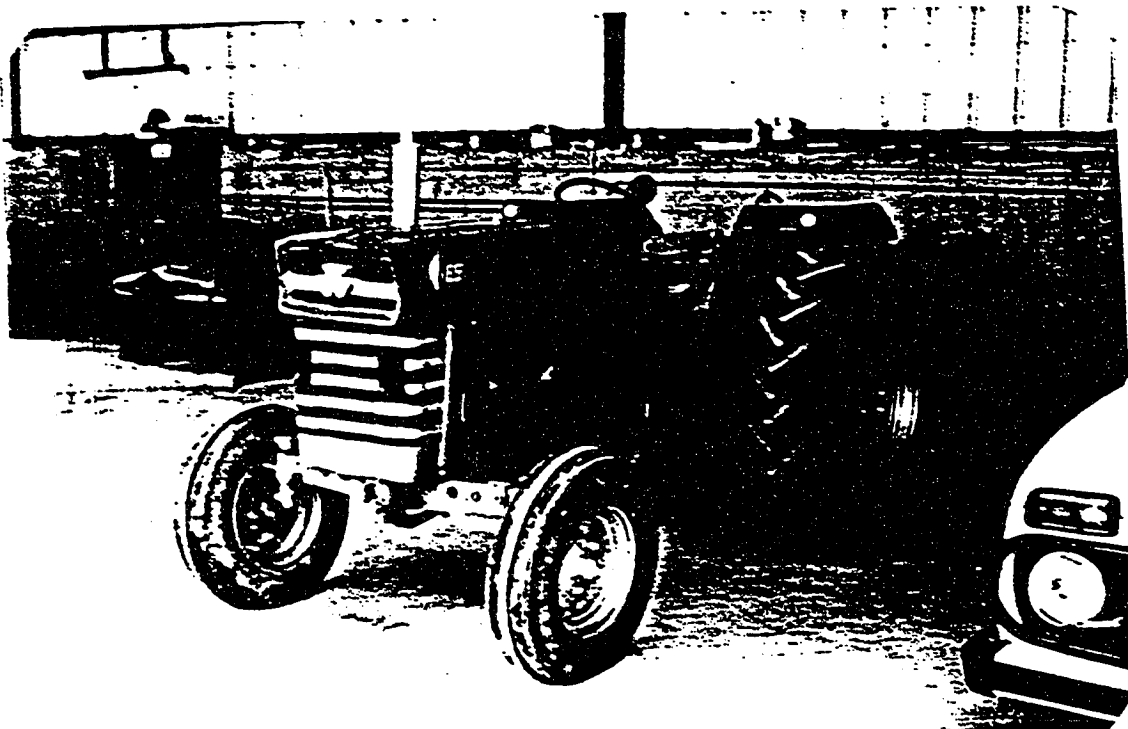
Saudi Aramco has used tractor with disc to cultivate Ras Tanura landfarm (Figure 4.4). These equipment were doing fine for the operation of the landfarm.

4.2.4 Soil Amendments

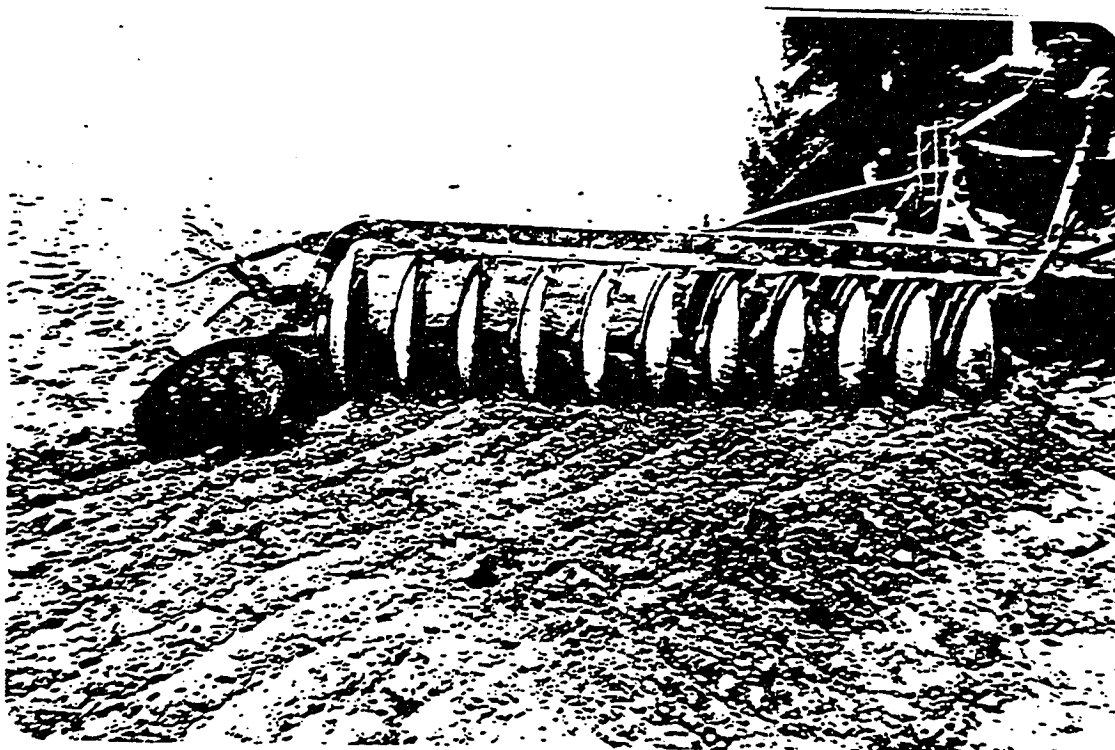
Water is the only amendment that Saudi Aramco used during the operation of Ras Tanura landfarm. Water had be trucked to the site once a month during summer time and less frequent during winter months. Soil moisture was maintained at a range of 10-15 % (wt)of water in the soil.

Figure 4.4
Equipment used at Ras Tanura Landfarm

TRACTOR



DISC



4.2.5 Monitoring Program

The monitoring program that was conducted at Ras Tanura landfarm was divided into two parts:

1. Operational Monitoring is conducted to find how well sludge decomposition is progressing and to establish need for any corrective action. Samples had been collected within three days after every four times of cultivation. Samples from incorporation zone had been collected to test for oil & grease, pH and moisture.
2. Environmental Monitoring is conducted two times per year to evaluate surface soil, surface soil and groundwater characteristics in order to verify compliance with proper facility operation, regulatory standards and environmental protection. Table 4.1 show the parameters that used to be test for during this part of monitoring program

Table 4.1
Environmental Monitoring Program

SAMPLE TYPE	SAMPLING TECHNIQUE	ANALYTICAL TEST	FREQUENCY
Soil			
Subsurface	Auger or corer	pH (<u>in situ</u>)	Semiannually
Surface	Grab sample	Cation Exchange Capacity (CEC)	"
		Oil Content	"
		Moisture Content	"
		Total Organic Carbon (TOC)	"
		Metals	"
		Available Nitrogen (NH ₄ , NO ₃)	"
		Nutrients	"
		Phenol (Subsurface only)	"
		Benzene (Subsurface only)	"
Soil Pore Water	Lysimeter or Pressure - Vacuum Soil water sampler	pH (<u>in situ</u>)	Quarterly
		Electrical Conductivity (EC)	"
		Oil Content	"
		Metals	"
		Phenols	"
		Hydrocarbon (HC)	"
		Total Organic Carbon (TOC)	"
Groundwater	Grab sample	Total Organic Halides	"
		pH (<u>in situ</u>)	"
		Electrical Conductivity (EC)	"
		Oil Content	"
		Metals	"
		Chlorides	Annually
		Phenols	"
		Hydrocarbon	"
		Sulfates	"
		Total Organic Carbon (TOC)	"
Sludge	Grab sample	pH (<u>in situ</u>)	"
		Oil Content	"
		Metals	"
		Solids	"
		Water (% H ₂ O)	"
		Phenols	"
		Hydrocarbons (HC)	"
		Cyanide	"

4.3 SAMPLING PROCEDURE

Sampling methodology is of paramount importance. The method chosen should be adhered to throughout the successive monitoring phases to insure analytical reproducibility. As a result of operating Ras Tanura Landfarm, Saudi Aramco has developed a comprehensive analytical procedures for soil, sludge and groundwater. All procedure which are followed at Saudi Aramco are USA EPA approved procedure.

Soil Sampling is accomplished by obtaining a minimum of 20 cores (using an open corer or screw auger) to insure complete and random coverage of the area. It is recommended to collect an individual sub-samples of 500-1000 grams per core and mechanically mix them to form a composite sample. Samples must be taken from the same locations in the field during each sampling. Therefore, sampling sites should be identified. Table shows Saudi Aramco recommended analytical techniques for soil.

Sludge should be sampled by combining a number of random samples to form a representative sample. It should be noted that sludge exists in layers and greater care should be taken in sampling. Table 4.2 shows tests that are required to be conducted for the received sludge.

For groundwater sampling procedure refer to "Manual of Groundwater Sampling Procedure" EPA Series, 1981.

Consistent techniques should be used in successive testing phases to establish a base line for comparison.

Table 4.2

Recommended Analytical Techniques for Soil

ANALYSIS	RECOMMENDED ANALYTICAL METHOD
% Oil	APHA 5520-D (1); Soxhlet extraction method.
Cation Exchange Capacity (CEC)	APHA 4500 (1); Ammonia Selective Electrode Method; for sample preparation use Std. Methods of chemical analysis; Krieger; 6th edition; Part B; Chapter 46 (soils); Page 2327.
% Moisture	APHA 2540-B (1); Total Solid Dried at 103-105 °C. or Loss on heating method
pH	APHA 4500-H (1); Electrometric Method or Method 9045 (Soil pH) (2).
Bacteria (Microbe)	SALAM-63.2; Enumeration techniques for microorganisms.
Available Nitrogen NH ₃ -N NO ₃ -N	For sample preparation see (3). APHA 4500 (1); Ion-Selective Electrode Method. ASTM-D 992; Cadmium Reduction Method.
Nutrients Phosphorus	ASTM-D515-82; Colorimetric Ascorbic Acid Reduction.
Total Nitrogen and Carbon	Carlo Erba CHN elemental analyzer.
Heavy Metals	ASTM-D-4698-92 or equivalent EPA approved methodology. For sample preparation see (4).
Phenols	APHA 5530 (1); Photometric Method.
BTEX	EPA Method 524.2 (Purgeable organic compounds in water by capillary column (5).
Total Organic Carbon	TOC by LECO carbon/sulfur analyzer or SALAM-334T; Determination of Total Carbon by LECO.

- (1) Standards Methods for the Examination of Water and Wastewater, 1989. (APHA)
- (2) EPA-Test Methods for Evaluating Solid Waste-SW-846, third edition, 1986.
- (3) Oily Wastes Land Farming Procedures (3810C).
- (4) SALAM-33; Nitric acid digestion by the Parr Bomb Procedure.
- (5) EPA-40 CFR 136 (7-1-91 edition) or equivalent EPA methods in reference (2).

CHAPTER 5: RESULTS AND DISCUSSION

5.1 ACCUMULATION OF HYDROCARBONS

Before using the landfarm site for other purposes, the Refinery Upgrade Project Team conducted an extensive cultivation to bring the oil content of the site soil to an acceptable limit ($\leq 3\%$). First, however, representative samples were collected from all sections of the landfarm. These soil samples were analyzed for pH, oil content and water content. The purpose of this sampling was to prepare a remediation procedure for the site. The sampling procedure did not include analysis for heavy metals or any other contaminants. This was because a comprehensive sampling effort had been conducted by the Laboratories Department earlier which showed that the landfarm site do not contain high levels of such contaminants (Table 5.1).

Based on the result of the soil analysis (Table 5.2), a remediation plan was prepared for the landfarm. First, the site was watered by using tankers to bring the moisture content to the required level ($>10\%$). The site was left for a couple days and then cultivated by using a tractor with a disk harrow. The purpose of the cultivation was to provide oxygen to the topsoil layer and increase the contact surface area between the microbial population and oily sludge. Soil cultivation was carried twice a month for six months.

Table 5.1
Chemical Analysis of Soil Samples from Ras Tanura Landfarm

Parameter	Concentration (ppm)			
	Depth*	0-1'	1'-3'	3'-5'
Lead		203	10	3
Chromium		43	20	16
Nickel		15	2	2
Cadmium		1	1<	1<
Copper		125	--	--
Vanadium		27	--	--
Zinc		220	--	--
Oil & grease		138050	8445	545
PCB		Not Detected	Not Detected	Not Detected
Chlorinated HCs		Not Detected	Not Detected	Not Detected
Asbestos		Negative	Negative	Negative

* Depth from ground surface (ft)

Table 5.2

Soil analysis before remediation

Sample #	Oil and Grease %	Moisture content %	pH
A2	8	4.4	7.5
A3	15.3	7.0	7.3
A4	14.1	1.1	8.2
B1	14.6	1.6	8.5
B2	10.8	3.3	7.5
B3	7.8	2.0	8.2
B4	19.7	12.4	7.7
C1	44.0	5.5	8.2
C2	13.9	2	9.4
C3	25.2	15.1	7.7
C4	8.8	1	8.6
C5	16.0	2.6	7.7

Watering of the site was done twice during this period. There was no need for any pH adjustment during the remediation activities. Soil sampling was conducted every month to check if biodegradation was progressing. Nutrients were not added during this period since the carbon-nitrogen ratio was close to the recommend level (50:1).

Figure 5.1 summarizes the oil biodegradation in the Ras Tanura landfarm site. It shows that the oil content dropped to less than 2% in six months. The half life for tank bottom hydrocarbons that were disposed at the landfarm was determined from Figure 5.1 to be about 60 days. The composition of hydrocarbon residue in the soil was not analyzed, however, there were few studies that explored this issue comprehensively (2, 4, 10). It was shown that most of the hydrocarbon residues consists of heavy aromatics and asphaltic components. Streoo et. (10) showed that half life of polynuclear aromatic hydrocarbon compounds with 4-rings or more is greater than 150 days. This means that a considerable amount of these compounds were not biodegraded at Ras Tanura landfarm during closure remediation.

The behavior of biodegradation of oily waste as shown in Figure 5.1 indicates that the oily waste is composed of paraffins and aromatics which agrees with analysis of the oily waste that being disposed at the site (Table 5.3). Figure 5.7 shows the typical relative biodegradation rates for paraffins, aromatics and asphaltenes. Figure 5.2 indicates that paraffins and aromatics are degraded more rapidly than resins and asphaltenes.

Figure 5.1
Biodegradation of Oily Waste at Ras Tanura Landfarm

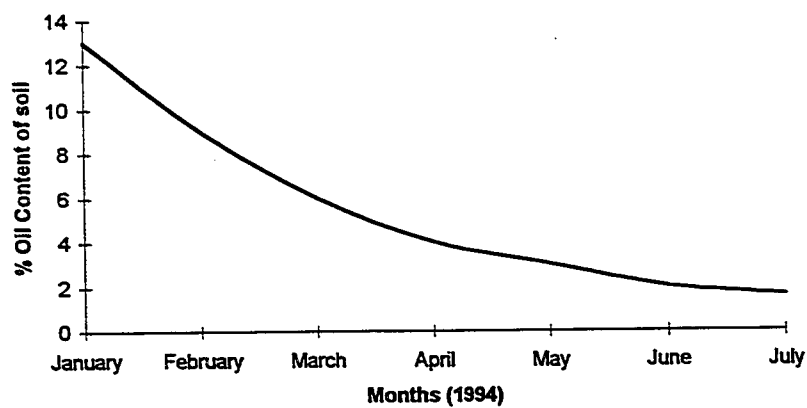


Figure 5.2
Typical relative degradation of various oil fractions (10)

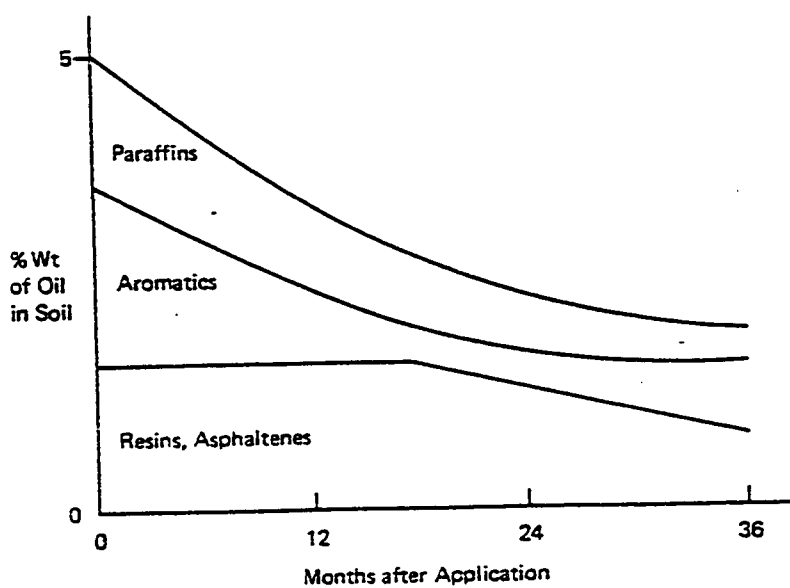


Table 5.3
Ras Tanura Oily Sludge Characteristics

	SLUDGE#1	SLUDGE#2	SLUDGE#3	SLUDGE#4	SLUDGE#5
WATER (wt.%)	3.3 (11.2) ³	1.5 (4.3) ³	5.9 (6.1) ³	19.5	14.7
OIL (wt.%)	77.6	74.3	60.2	24.5	3.9
SOLIDS (wt.%)	11.2	21.4	33.7	56.1	81.4
API GRAVITY	14.3	14.2	18.7	—	—
OIL EXT. COMPOSITION					
SATURATES ¹	38.8	33.8	38.0	—	—
AROMATICS ¹	37.1	36.5	35.7	—	—
RESINS ¹	18.2	23.3	24.9	—	—
ASPHALTENES ¹	5.9	6.4	1.4	—	—
PRISTANE/n-C17	0.26	0.26	0.28	—	—
PHYTANE/n-C18	0.44	0.46	0.47	—	—
LOSS-ON-IGNITION (wt.%) ²	97.5	90.1	95.3	42.4	9.0
CARBON (wt.%)	71	—	72	—	—
HYDROGEN (wt.%)	18	—	13	—	—
NITROGEN (wt.%)	<0.1	—	<0.1	—	—
OXYGEN (wt.%)	—	—	11.3	—	—
PHOSPHORUS (ppm wt.)	33.6	—	<50	—	—
METALS (ppm wt.)					
As	<0.5	—	<1	—	—
Ba	—	—	205	—	—
Cd	<0.5	—	<1	—	—
Cr	3.6	—	6.7	—	—
Cu	4.9	—	9.9	—	—
Pb	4.3	—	10	—	—
Mn	—	—	50	—	—
Hg	<0.5	—	<0.5	—	—
Ni	8.8	—	13	—	—
Se	—	—	1.5	—	—
Ag	—	—	<1	—	—
V	—	—	19.5	—	—
Zn	30.8	—	37	—	—

¹ wt.% in total extractable oil.

² wt.% on air-dried basis.

³ Data in parenthesis are determined by Karl Fischer titration.

5.2 BUILDUP OF HEAVY METALS

As experienced at other full scale land treatment facilities, oily waste application has resulted in an accumulation of metals in the zone of incorporation at Ras Tanura landfarm. Table 5.4 presents the maximum metal concentrations observed at Ras Tanura landfarm and background soil level from the Ju'aymah area. The background metals concentrations at Ju'aymah landfarm site has been used due to lack of background concentrations for Ras Tanura site. Ju'aymah landfarm has been constructed to replace Ras Tanura landfarm. Ju'aymah site is located 15 km north of Ras Tanura Refinery and the site soil has similar characteristics to Ras Refinery landfarm (i.e., sandy soil). Background concentrations were measured on soil where wastes had never been applied. The concentrations in the landfarm site soils are significantly higher than the background values for chromium, copper, lead and zinc.

Table 5.4

Metals concentrations at Ras Tanura landfarm and Ju'aymah area

Metal	Concentration at R.T. landfarm (ppm)	Concentration at Ju'aymah area (ppm)
Cadmium	1	1
Chromium	43	22
Copper	125	5
Lead	203	1.5
Nickel	15	10
Vanadium	27	12
Zinc	220	7

Figures 5.3, 5.4, 5.5, 5.6 and 5.7 show metals accumulation at Ras Tanura landfarm at different years. These figures show that after 1989 the accumulation rate is reduced compared to the accumulation rate during the previous period for cadmium, chromium and vanadium . This change may be due to reduction on generation of oily sludge from crude storage tanks. In 1987, Ras Tanura Refinery started using mixers at the crude storage tanks to reduce generation of oily sludge. Installing mixers at the crude tanks reduced the oily sludge generation to about 50% of the original amount. Application of less oily sludge has resulted in reducing heavy metal buildup at the landfarm. However, lead and zinc maintain the same accumulation rate for the period between 1985 and 1993. These two metals mainly produced in API separators oily sludge. The generation rate of this type of sludge has not changed during the landfarm operating life. Therefore, the buildup of lead and zinc at the landfarm was maintained at contact rate. This will not be continued after 1998 since the characteristics of API separators will change due to the addition of the new processes. The lead buildup will be less because of using MTBE instead of tetraethyl lead in gasoline production.

Figure 5.3
Buildup of Cadmium at Ras Tanura Landfarm

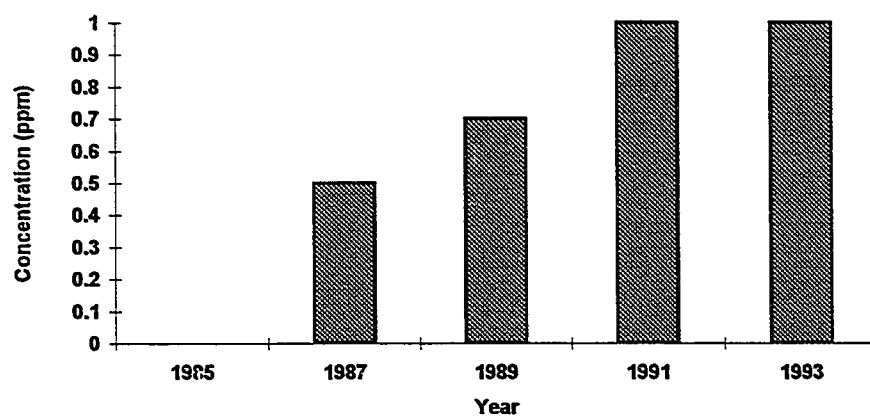


Figure 5.4
Buildup of Chromium at Ras Tanura Landfarm

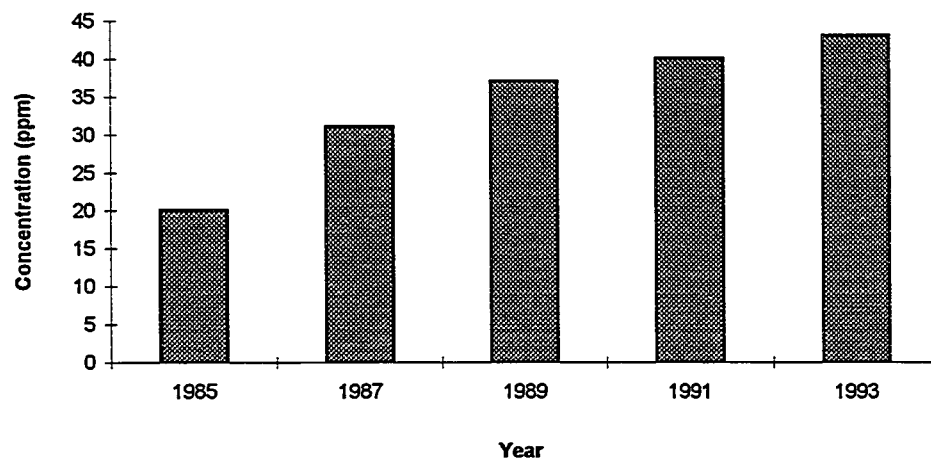


Figure 5.5
Buildup of Lead at Ras Tanura Landfarm

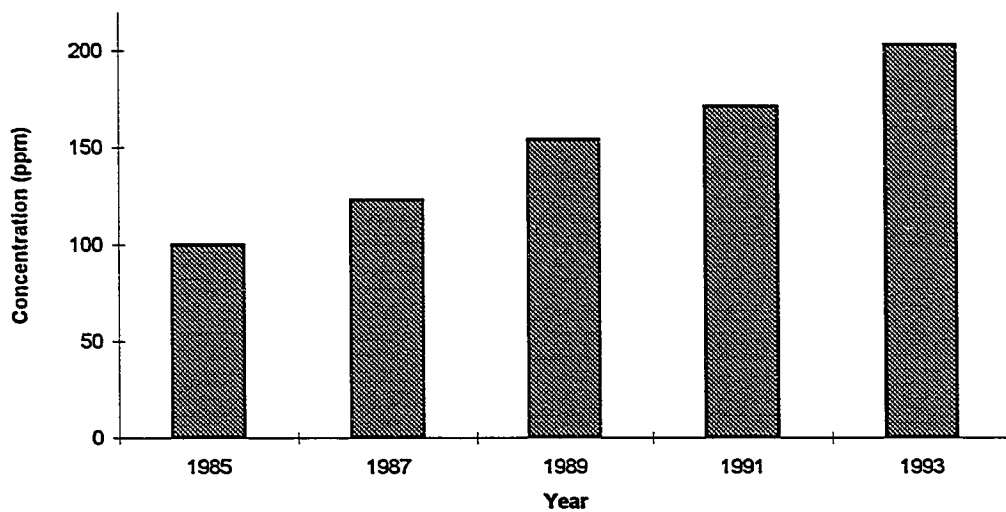


Figure 5.6
Buildup of Vanadium at Ras Tanura Landfarm

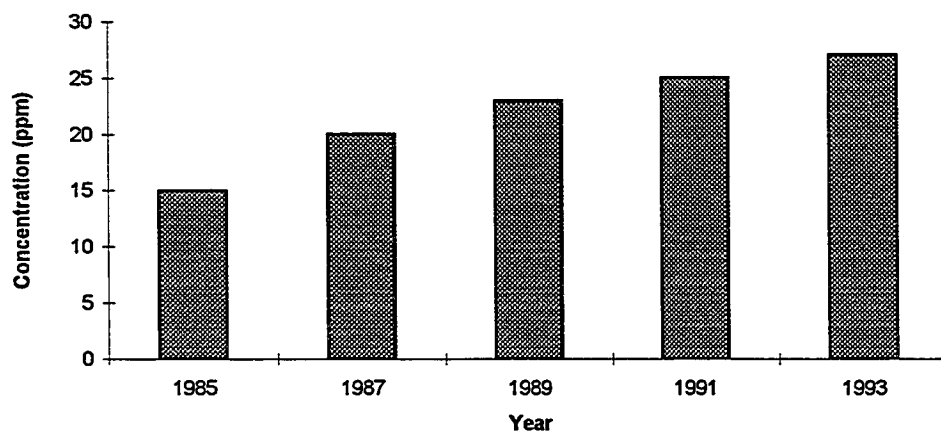
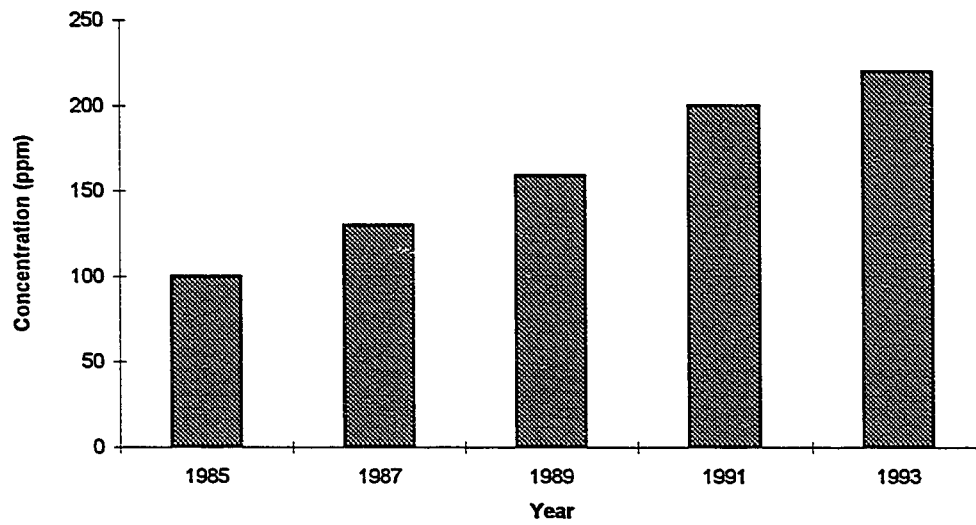


Figure 5.7
Buildup of Zinc at Ras Tanura Landfarm



5.3 DISCUSSION

5.3.1 Accumulation of hydrocarbons

Hydrocarbons accumulation and migration at Ras Tanura landfarm after 10 years of operation has shown to be less than the levels at similar landfarms which have been operated at United States. The oil content in the zone of incorporation at the Ras Tanura landfarm had been reduced to 1.7% (refer to Figure 5.1) before the closure of the site. In comparison, The oil content in the zone of incorporation at most U. S. full scale landfarms range between 3 to 10% with average of 4%. This shows that landfarming process in Saudi Arabia climate is promising method to treat oily waste sludge. One of the most important factors to accomplish high rate oil degradation is maintain the soil temperature at higher range. In Saudi Arabia, soil temperature is maintained at higher level during most of the year. This is not the case in United States where the temperatures go down during winter time.

The remaining 1.7% of oil at the landfarm soil is mainly composed of heavy aromatic and asphaltic materials. This conclusion is based on studies which have been carried in US and have shown that most of the hydrocarbon residues consist of heavy aromatic and asphaltic materials. Also, soil analyses of the Ras Tanura landfarm confirms this conclusion by showing no PCB and chlorinated hydrocarbons in the landfarm soil (Table 5.1).

Soil analyses show that hydrocarbons migration at Ras Tanura landfarm is negligible. At the 3'-5' depth zone, oil content in the landfarm soil is 0.05% (Table 5.1). In comparison, Figure 2.1 shows that the oil content in the same depth zone for various landfarms in United States is 0.5% which is ten times

the content in Ras Tanura landfarm. This is understandable, due to the difference in the climates. In United States, the climate is characterized of heavy rain in the most of the year which promotes the migration of the hydrocarbons to deeper zones. On the contrary, Saudi Arabia is arid country where migration of oil will not be promoted by rain water.

5.3.2 Buildup of Heavy Metals

Soil analyses show that heavy metals levels at Ras Tanura landfarm have increased after 10 years of operation. However, The buildup rate of heavy metals at the at Ras Tanura is less than the rates which are observed at similar landfarms at United States. Soil analyses from Chevron landfarms (Table 2.3) show that heavy metals concentrations have increased between 10 times (for copper) to 80 times (for lead) in ten years. Other US landfarms (Table 2.1 and Table 2.2) show that the concentration have increased by one to 70 times, however, the time over which the heavy metals have built up is unknown. In comparison, heavy metals concentrations at Ras Tanura landfarm have increased by only two times in eight years. This difference in buildup rate could be due to dissimilarity in oily sludge characteristics or inequality in sludge application rates at various landfarms.

In addition, a comparison has been made between the levels of metals in Ras Tanura landfarm and Permissible Clean Up Levels (PCUL) (Table 5.5) which are established for the U.S. state of Arizona soils because the soil characteristics are similar to those in Saudi Arabia. Saudi Aramco use PCUL concentrations to determine if remediation is desired at any industrial location

before any other activities (renovation, demolition, construction, etc.) can take place at the site. If any of heavy metals exceed the specified PCUL limit, the soil will be excavated and transported to proper disposal facility.

PCUL concentration can be used also in estimating the life time for the landfarm. For example if lead is assumed to be the limiting metal and buildup rate is assumed to be constant, the landfarm at Ras Tanura can be used for 24 years before the concentration reach PCUL limit (300 ppm).

Table 5.5

Metals concentrations
at R. T. landfarm and Arizona PCUL limits

Metal	Concentration at R.T. landfarm (ppm)	Permissible Clean Up Levels (PCUL) ¹ (ppm)
Cadmium	1	20
Chromium	43	800
Copper	125	500
Lead	203	300 ²
Nickel	15	500
Vanadium	27	200
Zinc	220	1,500

1. Permissible Clean Up Level (PCUL) for industrial locations in Arizona State.

2. Mean concentration for PCUL from different states for residential locations.

As shown in Table 5.5, the concentrations of heavy metals in Ras Tanura landfarm soil are far below Permissible Clean Up Levels.

Migration of heavy metals at Ras Tanura landfarm is minor compare to migration of these contaminants at US landfarms. For example, lead concentration at 3'-5' depth is 3 ppm at Ras Tanura landfarm whereas its concentration at the same zone is 19.5 ppm at US landfarms (Table 2.1). The concentration of 3 ppm which is determined at Ras Tanura landfarm could be the soil background concentration at this site.

In general, it is shown from the analysis of Ras Tanura landfarm data that the landfarming process did not cause any deleterious effects to the soil environment after 10 years of operation.

CHAPTER 6: CONCLUSIONS

The following conclusions were drawn from this study:

1. After 10 years of operation, accumulation of hydrocarbons in the zone of incorporation at Ras Tanura landfarm was minimal (1.7%) compared to other landfarming facilities in United States(3%).
2. Migration of hydrocarbons to deeper depth of the soil column at Ras Tanura was negligible (0.05% at 3'-5' zone).
3. Maximum oil degradation has been observed when the oil content of the soil ranges between 5% and 14%.
4. The half-life of tank bottom hydrocarbons is calculated to be about 60 days. Therefore, sludge application can be done 6 times a year in the same area provided proper landfarm operations/maintenance procedure are followed.
5. Buildup rates of heavy metals at Ras Tanura landfarm has shown to be less than the rates observed at US landfarms.
6. Migration of heavy metals to deeper depth of landfarm soil is negligible compared to migration of metals at US landfarms.
7. The Permissible Clean Up Levels (PCUL) of heavy metals for Arizona (U. S.) soils can be used to estimate the lifetime of a landfarm in Saudi Arabia.

CHAPTER 7: RECOMMENDATIONS

Based on the work performed to prepare this report, the following recommendations are made:

1. Background soil analyses for physical, chemical and microbial constituents should be performed prior to sludge application at the landfarm site. These analyses should be comprehensive to provide data on pre-operational conditions to be used in future for monitoring purposes.
2. To utilize the landfarm site properly, oil content should be kept higher than 5%. The optimum range of oil content has been determined to be between 5% and 20%.
3. For design purposes, PCUL limits should be used to estimate the lifetime of the landfarm and the economics associated with the establishment of the facility.

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