



## Project Summary

# An Evaluation of Subsurface Conditions at Refinery Land Treatment Sites

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Soil cores were collected from five land treatment facilities being used for the disposal of various solid wastes from oil refineries. Cores from similar but untreated soils adjacent to each facility were also collected for comparison. The samples were analyzed for chemical constituents to help determine the movement of wastes in the soil.

The selected sites represented diverse climatic regions, and the texture of the soils ranged from clay to sand. The facilities had been in operation from 1 to 7 years before sampling and had received a wide range of waste applications.

Data from this study indicate that metals from the applied waste typically remain in the treatment zone, and that concentrations generally are within ranges considered normal for soils. Only at one site (which had acidic soil) did chromium move to depths below the zone of incorporation. The potential exists for possible downward migration of land-treated hydrocarbons. At most sites, only very low concentrations of hydrocarbons were found at limited depths below the zone of incorporation. Since these materials remain in the aerobic zone, they are likely to degrade with time. At one site with sandy soils, hydrocarbons were detected at a depth of 224 cm (88.2 in.), where degradation would be expected to occur only very slowly.

*This Project Summary was developed by EPA's Municipal Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a*

*separate report of the same title (see Project Report ordering information at back).*

### Introduction

Land treatment has been demonstrated to be an effective method of disposing of waste streams that contain biodegradable organic materials. The various constituents of the land-treated waste that do not degrade accumulate in the soil, but some of these constituents could migrate down through the profile if the retention capacity is exceeded.

One waste category for which landfarming has been extensively used is oily refinery wastes. Such wastes come from wastewater treatment facilities, tank cleaning, or specific process facilities. The oil in these wastes is not effectively decomposed in anaerobic landfill environments, and the waste's water content typically makes incineration an expensive, fuel-consuming process. Thus landfarming has become an increasingly important mechanism for treating these materials.

Studies have indicated, however, that some of the components of oily wastes applied to soils are not completely degraded and may be mobile in the soil. Water quality could be adversely affected by saturated soil conditions or by overloading with high-BOD materials if contaminant solubilities are significantly enhanced. Such enhancement may occur as the result of reducing environments (unoxxygenated), soluble metal-organic complexes, or acidic soil conditions. The primary objective of this study was therefore to determine the potential for downward

migration of constituents following the long-term use of specific sites for land treatment of refinery waste sludges.

## Methods and Materials

### Site Descriptions

With the assistance of the American Petroleum Institute (API) task force, five sites were selected that had been used for land treatment of oily wastes for more than 5 years. Selections were based principally on geographical and climatological diversity. Because of the broad range of site characteristics (i.e., various wastes handled, application rates, soil types, and application methods), this effort should adequately reflect current refinery landfarming operations.

Site A comprises two experimental plots, approximately 1 acre each, within a larger enclosure. The terrain is rolling hills, and the elevation in the area ranges from 823 to 1189 m (2700 to 3900 ft). The native vegetation consists mainly of western wheatgrass, green needlegrass, and sagebrush. No cultivated vegetation existed on the site. The area has a 4- to 7-percent slope. The soil is a Kyle series consisting of a silty clay, well-drained, nearly level, gently sloping, and fine textured soil. The soil is moderately to strongly alkaline and occurs to a depth of 152 cm (60 in.), below which is clay.

Site B consists of roughly 2.4 ha (6 acres) and is located some 1.2 km (.75 mi) from a coast. The elevation is 152 m (500 ft) above sea level. The terrain includes upland and terrace depressions. Typical area vegetation consists of alsike and white clover, Italian ryegrass, Kentucky bluegrass, Douglas fir, and cedar. No cultivated vegetation existed on this site, which has a 1- to 2-percent slope. The land treatment soil samples revealed an undulating complex of Norma silty clay loam and Cagey silt loam. Both soils have a gravelly sand layer occurring at a depth of approximately 46 to 51 cm (18 to 20 in.). The Norma silty clay loam occurs to a depth of 198 cm (78 in.) and is slightly acid to a depth of 144 cm (58 in.), below which the soil is neutral to slightly alkaline. The Cagey silt loam occurs to a depth greater than 122 cm (48 in.) and is moderately acid to that depth, below which it is neutral to mildly alkaline.

Site C covers an area of about 2.4 ha (6 acres) and is surrounded by a 7.6-m (25-ft) concrete wall. The site is located in a lagoon area at an elevation of approximately 24 m (80 ft). Vegetation is typical of species occurring only on extremely disturbed areas. The slope is less than 0.5 percent. The soil is a Typic Xeropsamment mixed thermic (Oakley fine sand).

Site D lies on a nearly level coastal terrace with a slope of 0 to 1 percent, bordered on one side by a narrow strip of land with moderately and strongly sloping loamy soils. The site lies on top of a hill, and the vegetation consists of native and sprigged coastal Bermuda. The area is approximately 165 x 55 m (180 x 60 yd), and it is divided into 71 equally wide strips. A control strip occurs at each end, with alternating grass and treated strips in between. The soil is Miguel fine sandy loam consisting of deep, loam, and sandy soils containing moderate clay pan. The loam occurs to a depth of 76 to 138 cm (30 to 55 in.), and the pH ranges from 6.0 to 7.0 from the surface down.

Site E consists of a diked area surrounding a tank on the refinery site. The existing vegetation is 60-percent St. Augustine grass and 40-percent Bermuda grass. Some St. Augustine grass was grown on the site. The typical slopes were 0 to 3 percent, but the treatment area had up to 5-percent slope in places. The soil is a complex of Lake Charles and Urban Land. The soil consists of remnants of deep, clayey soils that have been altered by cutting, filling, and grading. The Lake Charles and Urban Land soil ranges from slightly acid to mildly alkaline, and it occurs to a depth of 188 cm (74 in.).

### Experimental Design

A sampling program was initiated to evaluate the presence of waste constitu-

ents in surface and subsurface soils. Samples were collected both from soils that had been treated with refinery wastes and from adjacent untreated soils. The samples were all collected from similar depths, and the results of the analyses were compared to determine the mobility of waste constituents. Groundwater and soil pore analyses were not conducted. A schematic diagram of the analytical system appears in Figure 1.

### Sampling

The sampling scheme was dictated by field conditions. Multiple soil cores were taken at each site and composites were made for various depth intervals. Analyses were made for the parameters of interest following transport of the samples to the laboratory. The samples were transported and maintained in cold storage until analyzed.

### Analysis

#### Soil Properties

Appropriate soil analyses were made to provide a data base for correlative interpretation of the overall study results. These included pH, specific conductance, texture, cation exchange capacity (CEC), and soluble and exchangeable cationic distribution. In addition, soils were analyzed for NO<sub>3</sub>-N, chloride, and sulfate by specific anion electrode techniques (Table 1).

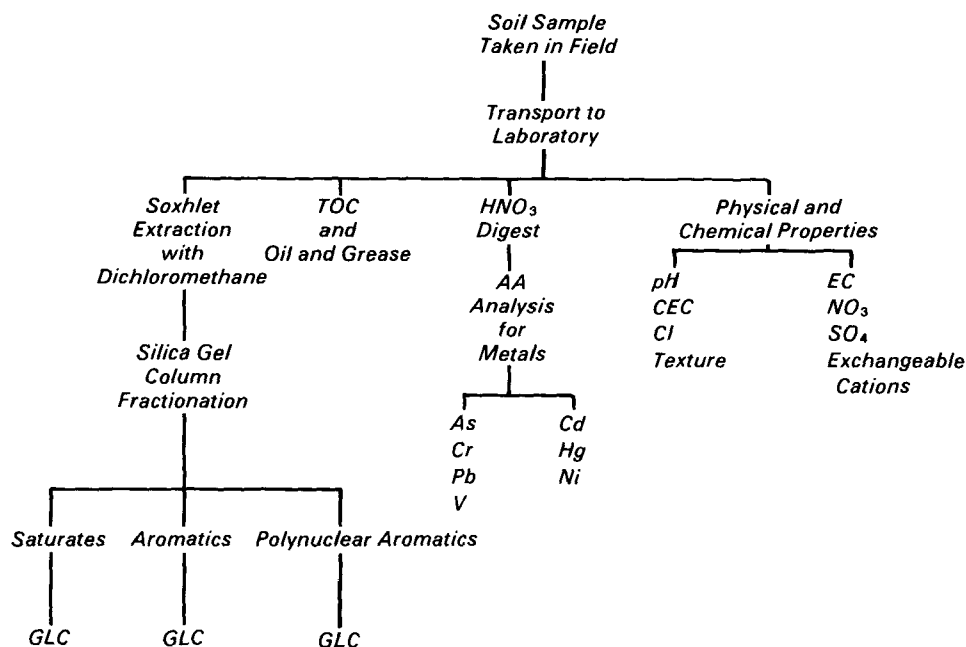


Figure 1. Schematic diagram of the analytical system.

**Table 1.** Mean  $Cl^-$ ,  $SO_4^{2-}$ , and  $NO_3^-$  Values Averaged Over Depth for Both Treated and Untreated Soils.

Site	$Cl^-$	Anion	
		$SO_4^{2-}$	$NO_3^-$
-----meq/liter-----			
A-Untreated	1.91	272	0.95
A-Treated	3.38	258	0.76
B-Untreated	0.67	9.54	0.54
B-Treated	2.51	31.6	1.08
C-Untreated	40.3	8.58	2.24
C-Treated	40.4	41.2	1.71
D-Untreated	60.8	13.7	9.01
D-Treated	29.5	12.8	16.8
E-Untreated	1.48	4.25	0.25
E-Treated	6.00	6.68	0.31

## Metals

Subsamples of each composite were digested with nitric acid and hydrogen peroxide. The latter was added to facilitate the destruction of organics and oxidation of the various metallic species. Following digestion, metals were analyzed according to EPA protocol. Atomic absorption spectroscopy was used for specific metal analyses, except for arsenic. Colorimetry was used for arsenic analysis following conversion to its hydride and complexing with silver diethyldithio-carbamate in a pyridine base. An aliquot of the metal digest was evaporated to a very low volume in the presence of a sulfuric/hydrochloric acid matrix to purge traces of nitric acid from the sample before arsine generation.

## Organics

In addition to the above inorganic soil properties and constituents, each segmented core was analyzed specifically for total organic carbon and extractable oil and grease.

Organics extracted from the first three depth intervals were subjected to column fractionation before gas chromatographic (GC) analysis. No attempt was made to fractionate organics in samples from lower depths before GC analyses because of relatively low extractable levels. Extracts were dried over anhydrous  $Na_2SO_4$  and reduced to a known volume by vacuum distillation. Methylene chloride was evaporated from an aliquot and gravimetrically assayed to determine the extractable residue level. Another aliquot was evaporated with a gentle stream of dry nitrogen, and constituents were resolubilized in hexane for loading onto a silica gel column and for subsequent fractionation

into saturates, aromatics, and higher condensed polynuclear aromatics.

Fractionation was achieved by loading a 0.2% solution of hydrocarbons onto 10 g of activated silica gel. The sample vial was rinsed with approximately 2 ml petroleum ether, and the rinse was transferred to the column. Saturates were then eluted with 25 ml of petroleum ether. The sample vial was rinsed with 2 ml of 20% methylene chloride in petroleum ether and loaded onto the column. Aromatics were then eluted with 50 ml of 20% methylene chloride in petroleum ether. A final rinse of the sample vial was made with methylene chloride, which was then loaded onto the column. This step was followed by elution of carbazoles and some higher condensed polynuclear aromatics. Last, the silica gel was rinsed with methanol to recover some of the higher-molecular-weight materials retained by the column. This fraction was analyzed by high performance liquid chromatography (HPLC).

Characteristic GC profiles were developed using a temperature-programmed Tracor Model 560GC\* equipped with a flame ionization detector. The GC was fitted with a 1.8-m by 0.65-cm (6-ft by 1/4-in.) ID glass column packed with 3% OV-1 on 80/100 mesh phrochromosorb W. Column temperature was programmed between 100° and 240°C at 3° C/min, with an initial hold setting of 10 min and a final hold of 40 min. Quantification was accomplished by comparing detector response (measured electronically) as an integrated peak area relative to the total carbon injected for known materials. A myriad of saturates, aromatics, and polynuclear aromatics were routinely used in assessing detector response.

## Results and Discussion

### Particle Size Distribution

Physical properties of a soil are defined as those characteristics, processes, or reactions of a soil that are caused by physical forces but are for all practical purposes integrally related to particle size. Site A reflects a medium-textured (loam) surface over a clay. Treated and untreated soils at Site B ranged from medium to coarse texture throughout the profiles. A coarse texture (sand) dominated the profile developed at Site C. Site D was typically medium textured, becoming coarser with depth. Site E can best be described as a heavy clay.

\*Mention of trade names or commercial products does not constitute endorsement or recommendation for use

### Cationic Distribution

The CEC is the total number of exchangeable cations that a soil can adsorb. Some of the calcium and magnesium reported as exchangeable cations exceed CEC values because of sparingly soluble sulfate or carbonate salts or both. CEC levels generally reflect corresponding clay contents.

Some of the treated sites have higher CEC values than their control areas, a fact that is attributed to organics in the wastes applied. High sodium saturations are generally reflected in both treated and untreated profiles. The data suggest that after these sites have been used in the land treatment of refinery waste sludges, only a slight alteration has occurred in the cationic distribution toward sodium. Some evidence shows that the sodium levels were attenuated through the land treatment of refinery sludge at Site A.

### Soil Reaction

Comparative soil reactions as pH profiles were developed for both untreated and treated soils at the respective sites. Site A demonstrates the typical acidifying effect of organics undergoing degradation in soil. The influence of land treatment on soil pH was mostly found to be attenuated within the upper 0.9 to 1.85 m (3 to 6 ft). Attenuation is reflected by convergence of the values for treated and native soils. The divergent profiles for Sites B and C are attributed to coarse soil texture and associated low buffering capacity (CEC).

### Soluble Constituents

The distribution of soluble cations found in the soil samples does not clearly relate to migration tendencies because of the complicated anionic interactions involving precipitatory mechanisms of less soluble species. The presence of soluble sodium salts within treatment facilities tended to decrease solution levels of background calcium and magnesium salts.

Profiles were developed for the electrical conductivities (EC's). Values generally reflected near-surface salt accumulation in waste-treated soils and downward migration in all but the more acid Site A. The extreme salinity noted between 0.5 and 1 m (1 and 3 ft) of the control soil at Site D indicated a subsurface saline seep (a natural phenomenon).

Chloride, sulfate, and nitrate anions were measured for each depth interval sampled and correlated to the corresponding EC value using the following multiple linear regression model:

$$EC = b_0 + (Cl^-) + b_2 (SO_4^{2-}) + b_3 (NO_3^-)$$

Computed values were linearly correlated with the observed values.

The data show that the variability of EC values can be described by a three-component anion model when EC is adjusted to a saturated paste value. Treated Site E did not conform well to a linear model ( $r^2 = 0.33$ ). The variability in EC measured for a 1:1 soil-to-water ratio was somewhat mitigated when the EC was converted to a saturated paste moisture level such that a linear model could not resolve subtle differences below 46 cm (18 in.).

Though somewhat scattered about the idealized regression line, the data demonstrate a strong positive correlation, which supports the fact that variability in EC with depth can be discerned by the changes in the respective anion concentrations. Data of this nature are always difficult to extrapolate, but the impact of salt loading from land treatment of refinery wastes does appear to be low.

### **Heavy Metal Distribution**

Trace minerals generally tend to have an enhanced soluble phase in soils with high organic contents — principally through chelation mechanisms. Under such conditions, mobility is controlled by soil surface adsorption and precipitatory mechanisms.

Chromium was significantly higher in all treated surface horizons. Compared with untreated background soils, lead was higher in all but Site E. The only other significant element detected was the mercury accumulated at treated Site B. Though chromium, lead, and mercury accumulated in significant quantities at one site, only the mercury level could be considered abnormally high relative to naturally occurring metal concentrations. Considering the low CEC of this site, the mercury concentration is probably at a maximum safe level.

No evidence showed the downward migration of metals, including those normally considered as anionic in character (As, Cr, V).

### **Organic Distribution**

An analysis of variance (ANOVA) using total organic carbon, oil, and grease as duplicate measures of the same parameter was used to evaluate hydrocarbon levels in treated and untreated soils and at various depths within sites. Hydrocarbon levels at Site A were significantly higher in the treated soil, with an F test indicating the difference to be significant at better than a 1-percent level. The least significant difference (LSD) computed for Site A was used to compare oil and

grease levels with depth at the treated site. This test suggested that oil and grease are retained within the surface 23 cm (9 in.) of soil.

The ANOVA for Site B indicated that the greater hydrocarbon levels in the treated soil were significant at a 1-percent level. Variance with depth was significant at the 5-percent level. Oil and grease at this site were attenuated within the top 60 cm (2 ft) of soil. No attempt was made to split out the variability because of the technique of measuring hydrocarbons from that of the error mean square. This technique reduces the sensitivity of assessing real differences in the hydrocarbon concentration as a function of depth.

Data evaluated for Site C do not reflect a statistical difference between hydrocarbon levels of treated and untreated soils but values decreased significantly with depth. Simple comparisons with the untreated soil are not possible because high hydrocarbon levels are present in the reference soil to appreciable depths.

Hydrocarbons at Site D reflect the general trends found at Sites A and B in that the treated soil differed significantly from the untreated soil. The organics were attenuated within the top 30-cm (1-ft) of the soil.

Site E reflected no statistical differences as a result of treatment, and correspondingly no differences with respect to depth. These data suggest that hydrocarbons loaded onto the soil have degraded without appreciable migration of degradation products.

### **High Performance Liquid Chromatography (HPLC)**

Surface horizons for all treated sites and subsurface samples showing significant hydrocarbons (detected by GLC flame ionization) were analyzed by HPLC. To help detect phenolic derivatives, analyses were made by injection of a methanolic extract of the sample. Extracts were generated by high-speed blending of sufficient sample to provide a detection limit of 1-ppm phenol, based on the integrated area of the standard.

Comparative retention time and area ratio analyses show only two surface samples and one subsurface sample that possibly contain phenolic materials. These are the immediate surface samples collected at treated Sites A and E and the 76- to 91-cm (30- to 36-in.) depth interval sampled at treated Site B. Though several phenolic derivatives fit the retention time criteria, only pentachlorophenol passed the area ratio test for the surface samples

at treated Sites A and E. Based on the detector's response to lindane, aldrin, dieldrin, heptachlor, and arochlor 1254, no halogenated hydrocarbons were detected in quantities exceeding 1 ppm. This result strongly suggests that material detected in the phenolic screening as potentially pentachlorophenol was something other than a chlorinated hydrocarbon.

### **Gas Liquid Chromatographic Characterization**

#### **Detector Response**

Gas liquid chromatographic (GLC) analyses were used in conjunction with column fractionation on silica gel to develop characteristic chromatograms of untreated and treated soil with respect to the depth interval sampled.

A complex mixture of standards was injected to evaluate GC column conditions and detector response over periods of a day, a week, and a month. The standard deviation reflects variability over a 4-month period and innate differences among compounds, particularly xanthene. A detector response of 10,000 integration units requires  $100 \text{ ng C} \pm 18 \text{ ng C}$  for Detector 1, and  $80 \text{ ng C} \pm 10 \text{ ng C}$  for Detector 2. Excluding xanthene does not numerically affect the standard deviation, so 10,000 integration units correspond to  $100 \text{ ng C} \pm 8.5 \text{ ng C}$  for Detector 1 and  $80 \text{ ng C} \pm 4.5 \text{ ng C}$  for Detector 2.

#### **Column Chromatographic Fractionation**

The standard fractionation on silica gel reflects the usefulness of this procedure for potentially reducing the complexity of chromatograms to evaluate the fates of the various classes of compounds contained in the wastes added to soils. Soxhlet extracts of samples collected at the first three depth intervals were subjected to column fractionation on silica gel. Fractions 2 and 3 were combined in a manner similar to that used for the standard before GLC analyses. Methanol was used as a final rinse in an attempt to extract higher condensed polynuclear aromatics (e.g., asphaltenes) not eluted with the other solvents. No attempt was made to use column fractionation on Soxhlet extracts of samples collected at the lower depth because of the relatively low hydrocarbon levels and the potential for lowered concentrations of hydrocarbons recovered in multiple fractions. Thus to improve the sensitivity level to hydrocarbons extracted from samples collected at the lower depths, chromatograms were developed for total extracts

following the removal of an aliquot for gravimetric analyses.

### Molecular Weight and Carbon Number

A linear regression model was used to describe the relationship between retention time (RT) and molecular weight (MW). RT corresponding to peak sensitivity for compounds used in the standard mixture and others (including naphthalene, biphenyl, methyl heptadecanoate, 1,3,5-triphenyl benzene, triphenylethylene, tetraphenylethylene, and 9,9-bifluorene) increased linearly with increased molecular weight. RT values averaged for multiple injections of known compounds with various molecular weights gave a regression coefficient ( $r^2$ ) of 0.84. These data suggest that hydrocarbons with less than 76 g/mole would be eluted with the solvent front under the same column and instrument conditions used for the standards. A 20-min increase in RT roughly corresponds to 5 carbons added in a chain configuration for saturates, or a benzene ring added for aromatics.

Similar results are reflected in the linear regression retention and carbon number. Again, the fit of the model is reflected in the high regression coefficient value ( $r^2 = 0.83$ ).

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*Carlton C. Wiles is the EPA Project Officer (see below).*

*The complete report, entitled "An Evaluation of Subsurface Conditions at Refinery Land Treatment Sites," (Order No. PB 84-102 169; Cost: \$14.50, subject to change) will be available only from:*

*National Technical Information Service*

*5285 Port Royal Road*

*Springfield, VA 22161*

*Telephone: 703-487-4650*

*The EPA Project Officer can be contacted at:*

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