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Project Summary

Closure Evaluation for Petroleum Residue Land Treatment

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Three oily residue land treatment sites to which no waste applications had been made for six months, nine months, and six years, respectively, were sampled to define existing conditions. Runoff, zone of incorporation (0-25 cm), and unsaturated zone (26-152 cm) samples were collected at each site during the 15-month study period.

A considerable variation in residual oil content existed at the three sites. Site 2, a well-managed operating site which had received no waste for six years, had a residual oil concentration of 2-3 wt.% in the zone of incorporation. Sites 1 and 3, which had received waste applications within the 12 months previous to this study, contained 5-6 and 8-9 wt.% residual oil, respectively. Oil concentrations greater than background were detected as deep as 45-50 cm at all sites with the highest concentrations being found at site 3. Average concentrations of oil in soil remained relatively constant at each site during the study period; however, large variations in oil content of individual core samples were found within each site. Possible contributing factors to this apparent lack of degradation were extended periods of extremely wet or dry soil, low available soil nitrogen levels giving extremely high carbon-to-nitrogen ratios, and the presence of persistent hydrocarbons. Thirteen or more organic priority pollutants were identified in samples collected at each site; however, only trace quantities were found below the zone of incorporation. Several of these priority pollutants also were identified in adjacent soil background samples.

Metals were immobilized in the top 25 cm of soil at all sites. Soil and soil pore water at each site contained high chloride levels.

Site 2 supported a lush growth of vegetation while sites 1 and 3 supported little or no vegetative growth.

Vegetation studies revealed that grasses were more tolerant than tree seedlings when planted in areas having an oil content of 5-6 wt.%. Root development was inhibited at levels of 4-5 wt.%. In areas having an oil content of 9-13 wt.%, survival rates for both were very low.

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

Introduction

Land treatment as a disposal method for petroleum residues from oil refinery operations has become popular in recent years, although the technique has been in use for 15 to 20 years. Several studies have been performed to determine the fate of the oil and metals at active land treatment sites. However, few studies have been carried out at closed sites to see if a long-term threat to ground water exists. The purpose of this study was to identify the potential long-term environmental impacts of immobilized metals and persistent organics at closed land treatment sites to which previous applications of petroleum residues had been made.

Both the zone of incorporation (0-25 cm) and the unsaturated zone (to a depth of 152 centimeters) were monitored for contaminants at each site selected for study. Soil and runoff samples from each site were analyzed for oil content, metals, and selected organic pollutants. Other parameters monitored included: pH, cation exchange capacity, soil texture, soil permeability, soil structure, nitrate and phosphate levels, and chloride ion concentrations.

A revegetation study was carried out at one of the sites to identify grasses or trees which would grow at land treatment sites and possibly aid in site recovery.

Experimental Procedures

Approach

Three oil refinery land treatment sites in Oklahoma were selected for this study. Inactive land treatment areas to which no waste had been applied for six months (site 3), nine months (site 1), and six years (site 2) were studied. Soil samples from depths from 0-25 cm and 25-51 cm were analyzed for oil content, metals, TOC, COD, pH, nutrients, chlorides, cation exchange capacity, and selected organic compounds. Soil core samples from the unsaturated zone at depths from 51-152 cm were analyzed for oil content, metals, and selected organic compounds. Soil pore water samples from a depth of 1.2 m were analyzed for oil content, metals, TOC, COD, and selected organics.

The 0-25 cm depths were sampled because the till zone usually extends to a depth of about 25 cm at most operating land treatment facilities. The 25-51 cm depth was sampled because analyses of preliminary samples at these sites showed the presence of oil in some areas.

Soil samples from the deeper unsaturated zone were analyzed to determine if any migration of pollutants had occurred. Samples of soil pore water were analyzed as a part of the unsaturated zone monitoring program to identify any pollutants which might pass through the unsaturated zone.

Oil content of the 0-25 cm and 25-51 cm zone samples was determined at selected intervals during the 15-month sampling period in an attempt to determine rates of degradation of residual oil following site closure. In addition, a part of each site was tilled to see if tilling enhanced the rate of degradation. No nutrients were added to the site soils during the study, except in those areas used for the revegetation study.

Table 1. *Organic Compounds Identified in Soil at Land Treatment Sites*

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

"x" denotes compound which was present.

The revegetation study was conducted to identify trees or grasses that would grow in oily soil to aid in the recovery of land treatment sites. The revegetation study was conducted only at research site 3. The growth characteristics of five tree species and four grass species were observed for one growth season.

Site Characteristics

The site soils were tested for selected priority pollutants. The compounds identified at each site are listed in Table 1. The priority pollutants present were primarily polynuclear aromatics and phenolics.

The soil at each site was sampled periodically over a 15-month period. A subarea at each site was tilled so that the rate of residual oil degradation in the tilled and the untilled sections could be compared and evaluated. Oil concentrations present in different core samples at each site indicated that a considerable variation in the oil content occurred across the site. The mean oil content concentration in the top (0-25 cm) and bottom (25-51 cm) layers of soil at the three sites is shown in Table 2.

The residual oil content at site 2 (2-3 wt.%) was significantly less than that at site 1 (5-6 wt.%) which was significantly less than site 3 (8-9 wt.%). Waste had not been applied at site 2 for approximately six years while sites 1 and 3 had received waste applications within the previous 12 months. No apparent degradation of residual oil occurred at any of the sites during the 15-month study period, which might be attributable to several noticeable factors: (1) the large variation in oil content for samples collected within any one site indicate poor application, mixing and/or sampling techniques; (2) during the project period, no nitrogen fertilizer was added to produce a carbon-to-nitrogen ratio more favorable for sustained microbial activity; (3) adverse weather during the project produced long periods

Table 2. Oil Content Data—Means

Date		Mean %	Std. Dev.	Variance
Site 1				
	**Background Top*	0.56	0.30	0.090
	**Background Bottom*	0.13	0.06	0.003
4/8/82				
	Top	4.90	1.52	2.30
	Bottom	0.64	0.35	0.12
12/1/82				
	Top	5.62	2.33	5.45
	Bottom	1.85	1.40	1.96
Site 2				
	**Background Top*	0.43	.152	.023
	**Background Bottom*	0.40	0.10	0.01
4/6/82				
	Top, tilled	2.63	0.96	0.92
	Bottom, tilled	0.78	0.37	.14
	Top, untilled	2.95	0.52	0.28
	Bottom, untilled	--	--	--
7/8/82				
	Top, tilled	2.58	0.95	0.902
	Bottom, tilled	1.08	.33	0.11
	Top, untilled	2.60	1.72	2.97
	Bottom, untilled	1.17	0.58	0.34
11/19/82				
	Top, tilled	2.93	1.46	2.14
	Bottom, tilled	1.46	1.31	1.72
	Top, untilled	2.65	1.67	2.79
	Bottom, untilled	1.08	1.14	1.29
2/16/83				
	Top, tilled	2.97	1.70	2.89
Site 3				
	**Background Top*	0.57	0.50	0.25
	**Background Bottom*	0.10	0.0	0.00
3/26/82				
	Top	8.7	2.90	8.42
	Bottom	2.7	4.57	20.85
6/7/83				
	Top	9.03	4.85	23.56
	Bottom	5.12	4.62	21.42

**Mean of all background concentrations.*

of saturated or dry soil conditions either of which might have inhibited microbial activity; and (4) the residual oil at each site contained a relatively high content of high-molecular-weight organic compounds which are more resistant to biotransformation.

The effect of tilling on the rate of degradation was evaluated at site 2. A statistically significant change in the oil content of the tilled vs. untilled sections could not be detected over a 14-month period. Potential degradation might have been inhibited by low nitrogen levels. Waste had not been applied to this site for over six years. Oil was still present in some locations at concentrations above background; however, the site soil supported a dense growth of lush vegetation.

The concentration of selected heavy metals in the soil at the sites was compared to background concentrations. At all sites, metals were present at levels above background. There was considerable variability in the metal concentration across the sites, as with the oil content concentrations. The actual concentrations of metals were low. The metals were concentrated in the top 25 cm of soil, with little or no vertical migration.

Soil acidity at the top (0-25 cm) and the bottom (25-51 cm) of site soil was determined to indicate the potential for solubilization of metals. The range of pH was from 7.1 to 7.5 at all sites.

The chloride ion concentrations of the site soils were higher than background at all three sites (Table 3). Only one set of determinations were made, so variation over time could not be observed. However, since the chloride ion concentration of the soil pore water decreased with time, the same trend could be expected for soil chloride ion concentration.

Total Organic Carbon (TOC) values for the sites are given in Table 4. The TOC values in the top (0-25 cm) of soil at all the sites were greater than background. The bottom (25-51 cm) sample at site 3 had greater TOC values than background. At site 2 the top sample had a higher TOC than background. Sites with the higher oil contents had correspondingly higher TOC values. The oil at site 3 extended well below the zone of incorporation. This correlated with the high TOC values of the bottom sample at site 3.

The unsaturated zone at each of the three sites was monitored for pollutants by core sampling below the zone of incorporation at depths between 51 cm and 152 cm, and by collecting pore water passing through the unsaturated zone.

Water passing through the unsaturated zone contained amounts of chloride (from 12 mg/l to 5,000 mg/l), and extractable oil and grease. Some metals appeared to be solubilized under the existing conditions at these sites. Even though the pH of the soil pore water and the soil in the top 51 cm was usually above 7.0, barium, zinc, iron, and manganese were all at fairly high concentrations in the soil pore water.

Table 3. *Soil Chloride Concentration*

Date	Top	Mean Cl^- Concentration (mg/kg) Bottom	Bkg T	Bkg B
Site 1				
6/30/82	119.6	103.3	17.6	15.4
Site 2				
7/8/82	28.0	33.1	13 7	2.9
Site 3				
11/4/82	72.6	101.5*	19.8	7.3

*Mean of 2 determinations

Table 4. *Soil TOC*

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

*Mean of 2 values.

Table 5. *Organics Present in Unsaturated Zone Cores*

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

The soil pore water also contained high levels of TOC and COD. The average COD/TOC ratio ranged from 3.2 to 3.5. At site 1 the COD values ranged from 400 to 2420 mg/l initially, then decreased with time. The COD at site 2 ranged from 335 to 990 mg/l initially and also decreased with time. An exception which did not follow the typical trend occurred at site 3, where the COD values first decreased and increased again toward the end of the research period.

Evidence for significant migration of oil or metals into the soil of the unsaturated zone (below 50 cm) was not found. Indications are that there was movement of trace quantities of organic priority pollutants into the unsaturated zone. The soil cores samples from the unsaturated zone contained some priority pollutants at concentrations in the low ppb range. More priority pollutants were present in the soil cores than in the soil pore water at sites 2 and 3, but not at site 1. The compounds identified in deeper soil cores and the soil pore water were generally different compounds and are listed in Tables 5 and 6. Several of these same compounds also were identified in background samples.

The site soils were characterized for texture, permeability, X-ray diffraction, and cation exchange capacity. Composite samples from each site and from areas adjacent to the sites were analyzed.

Grain size distribution for the soils were determined in accordance with ASTM designation D422-63(72) or AASHTO designation T-88-78. Site 1 was a silty loam, site 2 a sandy loam, and site 3 a clay. Standard laboratory permeability tests were performed on samples of the top 25 cm of soil. No significant difference between the permeability of the background soil and site soil was observed at any of the sites.

The X-ray diffraction analysis showed some changes in the soil structure. There was a masking of the montmorillonite and chlorite peaks. One explanation is that the oily residues penetrated the interplanar structures of the clays. There were changes in the intensities of the calcite, feldspar, dolomite, and quartz peaks. Generally, the major peaks either remained the same or diminished in intensity with increasing oil content. The exception to this trend was the calcite peaks which generally increased in intensity with increasing oil content.

The cation exchange capacity of both site and background soils was determined using the ammonium saturation method. At sites 1 and 2, there was an increase in

Table 6. Organics Present in Soil Pore Water

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

Table 7. Characteristics of Site Runoff

Site No.	COD (mg/l as O_2)	TOC (mg/l as C)	Oil and Grease (mg/l)
1	120	18	8.4
2	5	<5	10.8
3	540	495	35.8

Site 1 - untilled, no grass cover.
Site 2 - untilled, grass cover.
Site 3 - tilled.

CEC where oil was applied to the soil. However, at site 3, the CEC of site soil was lower than the background soil.

Runoff

Runoff samples were collected to determine if runoff from closed land treatment sites contained hazardous constituents. A 25-year, 24-hour storm for the region was simulated.

The COD, oil, and grease data (Table 7) show that the runoff from tilled areas contained more organic material than untilled areas. Runoff from the tilled areas was in contact with the oily soil for a longer period because the tilled area was more porous.

Aluminum and iron were in runoff from all three sites at higher concentrations than that of applied water.

Revegetation

The revegetation study involved both field and laboratory (environmental chamber) testing. Trees and grasses were planted at site 3 and monitored for growth and development characteristics for one season. The trees planted were black locust (*Robinia pseudoacacia*), hackberry (*Celtis occidentalis*), osage orange (*Maclura pomifera*), red cedar (*Juniperus virginiana*), Russian olive (*Elaeagnus angustifolia*). The grasses planted in the field were: bermuda grass (*Cynadon dactylon*), colonial bentgrass (*Agrostis tenuis*), crabgrass (*Digitaria sanguinalis*), weeping lovegrass (*Eragrostis curvula*).

The field site was divided into two oil level sections. One contained moderate amounts of oil (5-6%) and the other heavy amounts (9-13%). A control site which contained no oil was also established. Tree seedlings were placed in holes with a mixture of peatmoss and soil from the control area. This was to buffer the young roots from adverse effects of the waste until they were better established. The grasses were planted by broadcasting seed onto beds of processed cow manure and wheat straw. Bermuda grass was sprigged.

Crabgrass seed and bermudagrass sod were used for both environmental chamber and field studies.

With the exception of one red cedar, all trees in the heavily oiled area failed to survive. The survival rate was greater in the moderately oiled soil; however, the trees that lived were stunted. Red cedar trees showed best tolerance. Their ability to tolerate heat and drought was reflected by a higher survival rate.

Crabgrass and bermudagrass grew best in the field. There was a germination delay and biomass production when compared to the control soil. Oil and volatile waste products in the site soil are suspected to be responsible for the growth abnormalities.

Heavy amounts of oil had adverse effects on the vegetation. Drought resistant species fared best in the dry, hot climate. In addition to the species planted, a few native plants were observed growing in lightly oiled (1-5%) sections of the land treatment site.

Conclusions

1. Sampling procedures at land treatment sites must be carefully designed, since there can be considerable variability in oil concentrations across a site.
2. Management of closed land treatment sites, i.e., nutrient addition, etc., should continue following the last waste application until biotransformation of all organic hazardous constituents has occurred.
3. Some vertical migration of oil may occur at the land treatment sites, but this migration probably will not extend below 50 cm of the surface. In this study, no oil was present in the soil between 50 and 150 cm at any of the three sites.
4. Persistent organic priority pollutants in oily residue land treatment site soils consist primarily of high-weight polynuclear aromatic compounds. If management of closed sites is not maintained, movement of these pollutants into the unsaturated zone may occur.
5. Reduction of the oil content at land treatment sites to background levels may not be possible. One site in this study had been well managed, had no residues applied for six years, and supported profuse vegetative growth; yet this site still had an average oil content level between 2.5 and 3 percent. Thus, it may be more practical to reduce pollutant levels to the point where inhibition of vegetative growth and leaching, air emissions, or surface runoff of hazardous constituents are no longer problems.
6. If proper pH management is maintained, metals in land treatment site soils should be immobilized in the top 25 cm of the soil.
7. Volatile hydrocarbons may be emitted during the tilling process for an extended period of time after waste application has ceased.
8. Vegetative cover reduces the potential for contamination of runoff with site pollutants. Grasses provide the best vegetative cover. A ground cover using grasses can be established at oil concentrations of 4 to 5 wt.%; however, root develop-

ment and crop yield may be significantly inhibited.

9. Closed oily residue land treatment sites should be tilled at frequent intervals and nutrients applied until the oil concentration has decreased to a maximum of 3 percent prior to attempting to establish a ground cover using forage crops (grasses).

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Don H. Kampbell *is the EPA Project Officer (see below).*
The complete report, entitled "Closure Evaluation for Petroleum Residue Land Treatment," (Order No. PB 85-115 822; Cost: $19.00, subject to change) will be available only from:
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