# Final Technical Report

Hydrogeologic Analysis of Contamination and Evaluation of Remediation Alternatives— Fox Vacuum Site, Jasper County, Texas

(RRC Site No. 93-03-0019)

# by

Alan R. Dutton Jeffrey G. Paine Steven W. Tweedy

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Bureau of Economic Geology Noel Tyler, Director The University of Texas at Austin Austin, Texas 78713-8924

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#### EXECUTIVE SUMMARY

The Bureau of Economic Geology (BEG) investigated the Fox Vacuum site (RRC Site No. 93-03-0019) in Jasper County, Texas, during a 4-month study from July through October 1995. Historical aerial photos indicate the site was developed between 1958 and 1976. Contamination identified at the start of this study included a sulfuric-acid contamination plume (soil pH of 1 to 4) that had affected the quality of soil water and killed grass across approximately a one-half-acre (2,023-m2) area of an adjacent pasture. The site also was believed to have seven earthen pits, probably containing spent drilling mud. The depth of the acid contamination was unknown. The scope of the BEG study was to determine the source, present extent, and probable fate of the sulfuric acid contamination and to ascertain the volume and contents of the earthen pits. This report presents the results of that study, along with an environmental impact assessment, risk-based evaluation of cost-effective remediation alternatives, and recommendations for RRC action.

The acid-contamination plume was mapped using a nonintrusive electromagnetic-conductivity survey. Survey results were calibrated by core from three bore holes made at the site. Each of the earthen pits was sampled. Aerial photos and ground measurements were used to estimate the acreage of the pits.

Maps and tables presented in this report show that the acid contamination is confined to the uppermost 10 ft (3 m) of the surface soil and that the greatest contamination is within the uppermost 4 ft (1.2 m). Vertical movement has been restricted by soil texture and seasonal moisture content. The lateral extent of the acid contamination, moving toward the northwest

down the local hydrologic gradient, coincides almost exactly with the observed manifestation of stressed vegetation. The total volume of acid-contaminated soil is less than 516,432 ft<sup>3</sup> (11.9 acre-ft; 19,127 yd<sup>3</sup>; 14,625 m<sup>3</sup>). Crude-oil-contaminated drilling mud in the pits at the Fox Vacuum site makes up a volume of approximately 118,000 ft<sup>3</sup> (2.7 acre-ft; 3,000 yd<sup>3</sup>; 4,370 m<sup>3</sup>), but the low concentrations of total petroleum hydrocarbons (TPH), chloride, and barium in the mud are below regulatory levels.

The acid-contaminated soil can be cost-effectively remediated in place following methods long established for the restoration of acid mine soils and acid-sulfate soils in wetland-reclamation areas. No cleanup of the crude-oilcontaminated drilling mud is proposed. Application of 4,800 lb (2.2 metric tons) of finely ground calcitic limestone will neutralize the subsurface acid source and migrating plume and begin the process of soil restoration. An optional third stage of remediation is to restore the fertility of the soil and reseed grass to prevent further soil erosion. Cost of remediation will be less than \$5,000. Other alternatives, including excavation and landfill disposal, inplace soil flushing, and soil washing, will be 7 to 80 times as costly but will not ensure any better results.

#### INTRODUCTION

#### Statement of Problem

The Railroad Commission of Texas (RRC) has statutory responsibility under S.B. 1103 (72nd Legislature, 1991) for oversight of the cleanup of abandoned oil-field sites throughout Texas. Since 1991, RRC personnel have identified, inventoried, and ranked more than 100 abandoned oil-field sites as candidates for cleanup. The RRC ranking gives priority to contaminated sites that have had observable releases, that occur in ground-water recharge zones with high soil permeability, that lie near surface-water bodies or water-supply wells or both, that have high public profiles and have received complaints, and that are near population centers. Straightforward solutions for cleanup of surface contaminants are readily apparent for many of the sites. At other sites, however, outlining cost-effective approaches to site cleanup requires information on the less apparent subsurface extent of the contaminant and the location of contaminant sources.

For these sites, the Bureau of Economic Geology (BEG) is providing more extensive site investigations for the RRC under an interagency agreement. The purpose of these scientific investigations is to provide the required information for planning and executing an appropriate level of remediation.

At the request of the RRC, BEG investigated the Fox Vacuum site (RRC Site No. 93-03-0019) in Jasper County, Texas, 9.2 miles (15 km) south of Kirbyville and 8.0 miles (13 km) north of Buna, 0.4 miles (0.64 km) east of US Highway 96 on Alvarez Road (fig. 1). Contamination at the site that was identified at the start of this study included elemental sulfur in the site pad





and sulfuric acid in the soil zone (soil pH of 1 to 4) that had affected the quality of soil water and killed grass across approximately a one-half-acre (2,023-m2) area of an adjacent pasture. The area of barren ground with killed and stressed vegetation appeared to be increasing. The site also was known to have six small earthen pits and one large earthen pit, although the contents of the pits was poorly known. The site was brought to the attention of the RRC through a complaint alleging an impact on livestock.

# Objectives and Scope

The principal objectives of this investigation were to (1) identify solutions to meet RRC obligations to protect public health and safety and the environment and (2) limit potential cost to the State of Texas for cleanup by emphasizing nonintrusive and cost-effective techniques to define the extent of the problem. The investigation focused on determining the subsurface lateral and vertical extent of the sulfuric acid, identifying the volume and contents of the earthen pits, and evaluating cost-effective alternatives for managing the contaminants at the site.

The scope of work included (1) site environmental reconnaissance, (2) preparation of a Site Investigation Plan, (3) hydrogeological field investigation to determine the surface and subsurface extent of contaminant(s), (4) assessment of environmental impact, and (5) evaluation and recommendation of alternative cleanup options. We focused our study on the acid-contaminant plume and on characterizing the composition of the materials in the earthen pits. As part of the environmental assessment we considered exposure pathways. BEG visited the Fox Vacuum site in April 1995. The Site Investigation Plan was approved by the RRC in July 1995, and field measurements were begun and completed in August 1995. Field work

focused on mapping the site, conducting an electromagnetic conductivity survey to determine the subsurface distribution of acid, sampling affected and unaffected soils, sampling ground water in a shallow water well near the site, and sampling the contents of the earthen pits. A draft of this report was submitted for review by the RRC in October 1995. This final version was revised on the basis of comments received from the RRC and a peer review provided to the BEG.

Summary of Information on Fox Vacuum Site

A summary of what was known about the Fox Vacuum site at the start of the investigation is provided in the following paragraphs. This summary set the context for the scope of the site investigation to determine the extent of contamination, environmental impact, and appropriate remedial actions.

Site Description

The Fox Vacuum site, also referred to as the Buna Yard in RRC files (Site No. 93-03-0019), is in Jasper County, Texas, RRC District 3, approximately 9.2 miles (15 km) south of Kirbyville and 8.0 miles (13 km) north of Buna, and 0.4 miles (0.64 km) east of US Highway 96 on Alvarez Road (fig. 1). The present layout of the Fox Vacuum site is depicted in figure 2. This area is included on the Call Junction USGS 7.5-minute quadrangle map. Fox Vacuum Inc. is the last known operator of the Buna Yard (J. Tintera, personal communication, 1995). The site was apparently used as a washout yard for the vacuum truck service company and for drilling-mud disposal. In this document, the term Buna Yard refers to the facility within the property boundary shown in figure 2, and the term Fox Vacuum site refers to the Buna Yard as well as adjacent impacted properties under RRC jurisdiction for cleanup.



Figure 2. Map of the Fox Vacuum site showing locations and numbering of earthen pits and the position of the barren zone where pasture grass is absent. The site boundary and locations of pits were interpreted on the basis of 1976 and 1988 aerial black and white photographs. The barren zone was surveyed during August 1995. Not shown is a ditch along the east side of the site that connects pit 4 to pit 7.

A complaint (no. 03-4084) was directed to the RRC in 1993 after livestock were reportedly affected. RRC inspectors visited the site in August 1993 and February 1994, finding an approximately one-half-acre (2,023-m2) area of barren ground where vegetation had been killed. The barren ground included the Buna Yard driveway and extended as much as 60 ft (18.3 m) to the west, where pasture grass on adjacent property had been killed. The present landowner of the property west of the Buna Yard has chosen to curtail use of that pasture by his horses rather than risk their health and safety.

As part of their site inspections in 1993 and 1994, RRC personnel collected surface soil samples (table 1). Sample locations are shown in figure 3. Tests of soil samples indicated very low pH and elevated sulfate concentration (table 1). The contamination appeared to be sulfuric acid, suspected of being illegally discharged, although use of a solid-sulfur-rich waste product for the road base of the Buna Yard driveway is also a possibility. None of the metals reported in table 1 exceed risk-based soil cleanup standards designed to protect human health from exposure (for example, Title 31 of the Texas Administrative Code, subchapter S, appendix II, 1993). RRC has posted hazard warning signs on the gate barring the Buna Yard driveway and constructed a wire fence to isolate the affected part of the pasture. The RRC Special Response team then placed the Fox Vacuum site on its priority list of abandoned oil-field sites as a candidate for cleanup.

The history of industrial activity at the site is not well defined by available data. An aerial photograph shows that the area of the Fox Vacuum site was a clear-cut pasture in 1958 with no evidence of site development. Another aerial photograph shows that the Buna Yard was fully developed by 1976, with the driveway and earthen pits in place. Other parts of the site were

Table 1. Summary of RRC analyses on soil samples from the Fox Vacuum site (units of mg/L except total petroleum hydrocarbons and oil and grease in percent (%) and electrical conductivity in mS/m)

Map no.		1	2	3	4	5	6	7	8	9	9
Sample no.		A	В	С	D	S-1	S-2	S-3	S-4	S-5	S-6
Date collected		8/23/93	8/23/93	8/23/93	8/23/93	9/8/94	9/8/94	9/8/94	9/8/94	9/8/94	9/8/94
Depth (inches)	· · · · ·	Surface	Surface	Surface	Surface	0 to 2	0 to 2	0 to 2	0 to 2	0 to 5	18 to 24
Arsenic	TCLP	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Barium	TCLP	0.07	0.05	1.55	0.39	0.06	0.09	0.05	0.17	0.05	0.07
Cadmium	TCLP	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Calcium	1:1 extract	nr	nr	nr	nr	739.	688.	586.	218.	752.	243.
Chloride	1:1 extract	100.	367.	153.	20.	10.	8.	169.	16.	22.	46.
Chromium	TCLP	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Lead	TCLP	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Magnesium	1:1 extract	nr	nr	nr	nr	5.	10.	121.	22.	45.	81.
Mercury	TCLP	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002
Potassium	1:1 extract	nr	nr	nr	nr	<5.	<5.	<5.	<5.	31.	16.
Selenium	TCLP	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Silver	TCLP	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<ບ.01	<0.01	<0.01	<0.01
Sodium	1:1 extract	nr	nr	nr	nr	<5.	10.	83.	21.	23.	22.
Sulfate	1:1 extract	nr	nr	nr	nr	5357.	2058.	15,647.	5294.	18,131.	16,253.
Conductivity	1:1 extract	nr	nr	nr	nr	1900.	313.	970.	930.	3800.	1400.
Oil and grease	% dry solids	3.0	2.5	0.17	0.05	nr	nr .	nr	nr	nr	nr .
pH	1:1 extract	1.19	1.13	8.22	5.94	1.34	2.81	3.18	1.76	1.00	1.86
Total petroleum hydrocarbons		1.5	0.79	0.07	0.02	• nr :	nr	nr	nr	nr	nr

# Table 1. Summary of RRC analyses (continued)

Map no.		10	11	12	13	14	15	15	16	16
Sample no.		B-1	B-2	<b>B-3</b>	B-4	P-1	SS-1	SS-2	SS-3	SS-4
Date collected		9/8/94	9/8/94	9/8/94	9/8/94	9/8/94	6/20/95	6/20/95	6/20/95	6/20/95
Depth (inches)		0 to 2	0 to 2	0 to 2	0 to 2	0 to 6	0 to 3	4 to 8	0 to 3	4 to 8
Arsenic	TCLP	<0.01	<0.01	<0.01	<0.01	<0.01	nr	nr	nr	nr
Barium	TCLP	0.34	0.11	0.4	2.16	3.7	nr	nr	nr	nr
Cadmium	TCLP	<0.01	<0.01	<0.01	<0.01	<0.01	nr	nr	nr	nr
Calcium	1:1 extract	262.	676.	83.	16.	183.	nr	nr	nr	nr
Chloride	1:1 extract	49.	7.	208.	34.	483.	13.	3.	51.	5.
Chromium	TCLP	<0.05	0.16	<0.05	<0.05	<0.05	nr	nr	nr	nr
Lead	TCLP	<0.01	<0.01	<0.01	<0.01	<0.01	nr	nr	nr	nr
Magnesium	1:1 extract	41.	6.	7.	<5.	13.	nr	nr	nr	nr
Mercury	TCLP	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	nr	nr	nr	nr .
Potassium	1:1 extract	58.	<5.	<5.	<5.	125.	nr	nr	nr	nr
Selenium	TCLP	<0.01	<0.01	<0.01	<0.01	<0.01	nr	nr	nr	nr
Silver	TCLP	<0.01	<0.01	<0.01	<0.01	<0.01	nr	nr	nr	nr
Sodium	1:1 extract	31.	<5.	5.	11.	771.	9.	5.	33.	5.
Sulfate	1:1 extract	896.	1686.	213.	20.	911.	357.	119.	1606.	283.
Conductivity	1:1 extract	180.	250.	54.	23.	380.	74.	32.	220.	58.
Oil and grease	% dry solids	nr	nr	nr	nr	nr	nr	nr .	nr	nr
pH	1:1 extract	3.67	3.47	4.18	4.57	7.9	3.69	0.32	3.40	3.61
Total petroleum		nr	nr	nr	nr	nr	nr	nr	nr	nr

hydrocarbons

# Table 1. Summary of RRC analyses (continued)

Map no.		17	17	18	18	19	19	20	21	22
Sample no.		SS-5	SS-6	<b>SS-7</b>	SS-8	SS-9	SS-10	Pad A1	BD-A2	BD-A3
Date collected	1	6/20/95	6/20/95	6/20/95	6/20/95	6/20/95	6/20/95	8/17/95	8/17/95	8/17/95
Depth (inches)		0 to 3	4 to 8	0 to 3	4 to 8	0 to 3	4 to 8	surface	0 to 3	4 to 8
Arsenic	TCLP	nr	nr	nr	nr	nr	nr	nr	nr	nr
Barium	TCLP	nr	nr	nr	nr	nr	nr	nr	nr	nr
Cadmium	TCLP	nr	nr	nr	nr	nr	nr	nr	nr	nr
Calcium	1:1 extract	nr	nr	nr	nr	nr	nr	nr	nr	nr
Chloride	1:1 extract	13.	3.	10.	2.	15.	9.	nr	nr	nr
Chromium	TCLP	nr	nr	nr	nr	nr	nr	nr	nr	nr
Lead	TCLP	nr	nr	nr	nr	nr	nr	nr	nr	n
Magnesium	1:1 extract	nr	nr	nr	nr	nr	nr	nr	nr	nr
Mercury	TCLP	nr	nr	nr	nr	nr	nr	nr	nr	nr
Potassium	1:1 extract	nr	nr	nr	nr	nr	nr	nr	nr	nr
Selenium	TCLP	nr	nr	nr	nr	nr	nr	nr	nr	nr
Silver	TCLP	nr	nr	nr	nr	nr	nr	nr	nr	nr
Sodium	1:1 extract	7.	5.	6.	5.	15.	5.	nr	nr	nr
Sulfate	1:1 extract	274.	122.	200.	83.	489.	134.	nr	248.	868.
Conductivity	1:1 extract	64.	32.	50.	23.	100.	34.	nr	57.	150.
Oil and grease	% dry solids	nr	nr	nr	nr	nr	nr	21.	nr	nr
рН	1:1 extract	3.82	4.04	4.4	4.45	3.76	3.97	nr	6.05	4.15
Total petroleum hydrocarbons		nr	nr	nr	nr	nr	nr	18.	nr	nr

nr not reported



also were composited.

heavily overgrown with trees, shrubs, and vines typical of the area. In the 1976 photograph, pits 1, 2, 3, 4, 6, and 7 appear active (fig. 2). The appearance of the site in the aerial photographs does not significantly differ between 1976 and 1988. The site is believed to have been abandoned in 1985, according to RRC files. Oil-field-related activities at the site, therefore, began sometime between 1958 and 1976 and ended perhaps as recently as 1985.

Raised earth berms surround pits 1, 2, 3, 6, and 7 but are less obvious around pits 4 or 5. The west, north, south, and east boundaries of the Buna Yard also are bermed. Site inspection found a dug channel extending east from pit 4 to the eastern boundary berm, then turning north and running to the eastern end of pit 7. The area of barren ground includes the main driveway of the site and part of the adjacent pasture to the west (fig. 2). Between the barren ground and the apparently unaffected pasture is a zone where grass is stressed (fig. 2), that is, grass is thinner, patchier, more yellow, and shorter than in the unaffected part of the pasture. Physiological stress to pine trees and shrubs growing in the raised earth berm on the west boundary of the site also is suggested by yellowing and thinning of needles and leaves and less annual new growth compared with that of pines off site. The berms around the pits on the east side of the site are heavily overgrown with shrubs and small trees, which seem unaffected. Pits 2, 3, 6, and 7 do not support shrubs or trees, whereas the surface of pits 1, 4, and 5 are at least partly overgrown.

Regional Hydrogeology

Table 2 lists records of wells and water levels obtained from computer files at the Texas Water Development Board (TWDB) and supplemented with

No.	Well ID	Aquifer unit	Depth (ft)	Date drilled	Water depth (ft)	Date measured	Land surface (ft)	Water elevation (ft)
1	Unnamed	"Montgomery"	25.7		4.9	4/25/95	108	103.1
		<b>H</b>		M	13.1	8/09/95	108	94.9
	•		•		12.8	8/16/95	108	95.2
2	6225504	"Montgomery"	29	1938	25.2	5/17/38	110	84.8
3	62-25-501	Chicot	212	1953	48.3	6/12/64	112	63.7
4	62-25-502	Chicot	199	1953	52.5	6/12/64	111	58.5
5	62-25-505	Chicot	388	1934	11	11/29/29	110	99.0
6	62-25-503	Chicot	260	1950	36.8	6/17/60	100	63.2
7	62-25-601	Oakville	1441	1945	43.2	7/06/60	105	61.8
			•		9.5	2/23/94	105	95.5

Table 2. Summary of information on water wells located within 1.5 miles of the Fox Vacuum site.



Figure 4. Locations of wells within 1.5 miles of the Fox Vacuum site as identified in TWDB files and field inventory. See table 2 for data on numbered wells; only location is given in TWDB files for wells shown without numbers.

file data from the Texas Natural Resources Conservation Commission (TNRCC) Central Records and with results of a field inventory during this investigation. Figure 4 locates wells within 1.5 miles (2.4 km) of the Fox Vacuum site.

The Fox Vacuum site lies in the outcrop of the Montgomery Formation (Shelby and others, 1992). Sand deposits of the Montgomery, the underlying Bentley and Willis Formations, and the overlying Beaumont Formation make up the Chicot aquifer in Jasper County (Wesselman, 1967; Baker, 1979; Ryder, 1988). The Chicot aquifer in the vicinity of the Fox Vacuum site might be composed of less than 25 ft (7.6 m) of sand, based on operational mapping unit II of Guevara-Sanchez (1974), which corresponds to the stratigraphic section making up the Chicot aquifer. The net thickness of sands within the aquifer varies according to the geologic environments in which the sand was deposited. Sands in the Chicot aquifer beneath the Fox Vacuum site were deposited in a sand-poor interchannel sedimentary basin (Guevara-Sanchez, 1974). The main fluvial-channel deposits lie to the west and east of the site, where the net thickness of sands is more than 75 ft (23 m).

Data presented by Wesselman (1967) indicate that the regional potentiometric surface of ground water in the Chicot aquifer dips toward the south at a gradient of 0.0007. The small gradient suggests that the Chicot aquifer is confined. The gradient also suggests that ground-water flow in the Chicot aquifer regionally is southward from the main recharge zone for the Chicot aquifer, which is inferred to be in the outcrop of the Willis and Bentley Formations north of Kirbyville (fig. 1). Beneath the Fox Vacuum site, the regional potentiometric surface lies at about 60 ft (18 m) above sea level, or at a depth of approximately 40 ft (12.2 m) below ground surface.



Figure 5. Vertical profile of hydraulic head in a transect along US 96 near the Fox Vacuum site. The thickness of the water column in a well is the waterlevel elevation minus the elevation of the well bottom. Hydraulic head is posted for contouring as if it were measured at the base of wells, which are assumed to have short screened intervals. Head data include measurements made between 1938 and 1990. Ephemeral water-saturated soils perched above the water table in the Montgomery Formation are not shown. Wesselman (1967) shows that south of Kirbyville the Chicot is a confined aquifer, that is, water levels in wells completed in the Chicot aquifer are artesian and rise above the elevation of the sands in which the water is found. The area where the aquifer is confined coincides with the distribution of the Montgomery Formation. The more abundant clay content of the Montgomery Formation apparently locally confines (pressurizes) the more permeable sands of the Willis and Bentley Formations. While the Montgomery Formation is classified as part of the Chicot aquifer, its clay content probably limits its contribution to the aquifer.

Figure 5 depicts the vertical and lateral gradients in hydraulic head within the vicinity of the Fox Vacuum site interpreted on the basis of water level and well depth data. Ground water within the Montgomery Formation has the potential to move downward toward the main part of the Chicot aquifer. Flow near ground surface also has a "downslope" component. For example, the Fox Vacuum site lies near a local surface water divide between Deer Creek and an unnamed tributary of Nichols Creek; ground water flows downward and laterally toward those creek bottoms where it might discharge. The predominant direction of flow within the lower, confined part of the Chicot aquifer is essentially horizontal and southward, which is consistent with the map view shown by Wesselman (1967, fig. 21). It also is possible that ground water moves upward from the Evangeline aquifer to the Chicot. Although true on a regional scale, especially near the coast (Ryder, 1988), little data exist in the plane of the profile shown in figure 5 to determine the local vertical gradient within the Evangeline. The vertical gradient between ground water in the Chicot and in the adjacent units most likely has been increased by drawdown of water pressure by wells in the Chicot.

Many shallow wells in the Montgomery Formation in the study area have a large diameter and most likely were "hand dug," rather than drilled, prior to the 1950s (Mace, 1994). One shallow, 2-ft- (0.6-m-) diameter, 25.7-ft (7.8-m) deep, hand-dug well in the Montgomery (no. 1, fig. 4) is within 350 ft (106.8 m) of the eastern boundary of the Fox Vacuum site. This well is not down-gradient of the Fox Vacuum site. Depth to water below ground surface declined in this well from 4.9 to 13.1 ft (1.5 to 4.0 m) between April and August 1995, most likely reflecting the seasonal decrease in effective precipitation and recharge. Water levels measured in this well (table 2) were not static but were affected by pumping for the household water supply. Other water wells located along Alvarez Road mostly are deeper wells in the Chicot aquifer. Soil Characteristics Soils at the Fox Vacuum site are mapped as part of the Kirbyville-Neitsch (1982):

Waller association, typified by deep, loamy, acidic, upland soils. According to "... Kirbyville soils have a surface layer of medium acid, gravish brown fine sandy loam about 5 inches thick. The next layer to a depth of 18 inches is strongly acid, very pale brown fine sandy loam. The upper part of the subsoil to a depth of 35 inches is strongly acid, light yellowish brown sandy clay loam that has pockets and streaks of very pale brown fine sandy loam. The lower part of the subsoil to a depth of 75 inches is strongly acid and very strongly acid sandy clay loam that is strong brown in the upper part and brownish yellow in the lower part" (p. 27)

"... Waller soils have a surface layer of strongly acid, very fine sandy loam about 6 inches thick. It is dark grayish brown in the upper part and grayish

brown in the lower part. The next layer to a depth of 16 inches is strongly acid, light brownish gray very fine sandy loam. The upper part of the subsoil to a depth of 31 inches is very strongly acid, light brownish very fine sandy loam. The lower part of the subsoil to a depth of 64 inches is very strong acid clay loam that is light brownish gray in the upper part and gray in the lower part" (p. 27–28).

Consistent with the regional interchannel setting defined by Guevara-Sanchez (1974), Kirbyville and Waller soils are poorly drained, have moderate permeabilities, a high water table at a depth of 1.5 to 2.5 ft (0.46 to 0.76 m), and soil pH of 4.5 to 6 (Neitsch, 1982, p. 28 and 186). The acidic Kirbyville and Waller soil minerals have low acid neutralization potential. The shallow zone of saturated ground most likely reflects a perennial perched water table in poorly drained soils lying above both the unconfined water table in the Montgomery Formation and the regional potentiometric surface of the Chicot aquifer.

#### **METHODS**

Field activities at the Fox Vacuum site included marking location control points, conducting detailed geophysical surveys, augering and coring bore holes for soil analyses, collecting pit samples for compositing and analyses, and collecting water samples from adjacent properties.

# Mapping

Lines for 11 geophysical surveys (fig. 6) were laid out across the site pad, pit berms, and adjacent pasture including the vegetation kill zone. Lines A through G are oriented north-south and lines H through K are oriented generally east-west (fig. 6). They form a grid that is weighted toward the area





showing surface evidence of contamination. The survey lines in the pit area and along the east site boundary were positioned along lanes cleared of dense brush.

Locations of the geophysical survey lines and their intersections were recorded by using conventional plane table and alidade surveying. The edge of the barren ground was also recorded. Survey accuracy proved acceptable; the best closure was 1-mm vertical deviation and <0.3-m lateral deviation at one station, and the worst closure was 4.25-m lateral deviation at another station.

Map data analysis consisted of digitizing the field survey map and superposing the survey lines on a digitally scanned aerial photograph. Coordinates (x, y) of stations along the surveys lines at which ground conductivity was measured were then calculated relative to an arbitrary origin (0, 0) on Alvarez Road. The x-y coordinates provided a base map for posting and contouring electrical conductivity values in plan view and for obtaining accurate site dimension data.

#### Electromagnetic Induction Survey

Electromagnetic induction surveys were conducted to identify variations in ground conductivity across the Fox Vacuum site that might be associated with sulfuric acid content in soils and possible salt water in pits at the site. At the start of the investigation, the depth to which acid had migrated was unknown and was a principal concern. Therefore, successive electromagnetic surveys were run to determine any conductivity changes with depth that might be related to acid infiltration. To establish background conductivity values, some profiles were acquired in areas expected to be

uncontaminated and most lines across contaminated areas were extended beyond the point where there was no surface evidence of contamination.

Electromagnetic induction methods (Parasnis, 1973; Frischknecht and others, 1991; West and Macnae, 1991) are used to measure apparent ground conductivity, which can be a proxy for ground-water conductivity and an indirect measure of the ionic content of ground water. Electromagnetic induction methods use a changing primary magnetic field created around a transmitter coil to induce a current to flow in the ground, which in turn creates a secondary magnetic field that is sensed by the receiver coil. In general, the strength of the secondary field is proportional to the conductivity of the ground. An assumption inherent to the method is that the near-surface environment consists of horizontal layers of infinite lateral extent. This is not strictly true directly beneath the Fox Vacuum site, where the contaminant is concentrated in and around the Buna Yard, but away from the yard the nearsurface layers probably do have sufficient lateral extent to render this assumption valid at the scale of investigation.

# Lateral Ground-Conductivity Surveys

The surveys were run in August 1995 along the 11 lines at the Fox Vacuum site (fig. 6). A Geonics EM34-3 ground-conductivity meter measured apparent conductivity (McNeill, 1980a). The EM34-3 supports separations of 32.8, 65.6, and 131.2 ft (10-, 20-, and 40-m) between the transmitter and receiver coil (fig. 7) and two principal coil orientations (horizontal dipole and vertical dipole). In the following text, these three surveys will be referred to using the metric distance, for example, the 10-m, 20-m, and 40-m surveys. All three coil separations were used, resulting in an effective penetration depth of 19.7 to 82 ft (6 to 25 m) for the horizontal dipole orientation and 39.4 to 164 ft (12 to



Figure 7. Model of ground-conductivity surveys. (a) Effective exploration depths at various coil separations and orientations of the Geonics EM34-3 meter. (b and c) Apparent lateral shift in conductivity resulting from survey across lateral discontinuities in conductivity.

50 m) for the vertical dipole orientation. Station spacing was 16.4 ft (5 m) for all lines. Conductivity values represent "bulk" conductivities, or an average conductivity of the soil volume beneath the transmitter and receiver coils, and are plotted on profiles and on maps at the midpoint between the transmitter and receiver coils.

During the electromagnetic survey, 589 ground-conductivity measurements were made at the Fox Vacuum site. Conductivity measurements were made as follows: (1) the transmitter coil was placed on the ground in the horizontal dipole orientation at a chosen station along a line; (2) the receiver coil was placed on the ground approximately 32.8 ft (10 m) from the transmitter coil; (3) the receiver coil position was adjusted until the separation meter on the receiver indicated the proper separation; (4) apparent conductivity was read from the meter in units of millisiemens per meter (mS/m) and logged on a digital data logger; (5) both coils were realigned in the vertical dipole orientation at the same station locations and coil separation; (6) apparent conductivity for the vertical dipole orientation was read from the meter and logged; and (7) the transmitter and receiver coils were moved 16.4 ft (5 m) along the line to the next station. The entire process was then repeated until the line was completed. After data were collected along a line for the 10-m coil separation, conductivity measurements were taken along each of the lines again for the 20-m and 40-m coil separations. Station spacing was 16.4 ft (5 m) for each of the three coil separations.

Vertical Ground-Conductivity Surveys

The effective penetration depth of the field generated by the EM34-3 increases with coil separation for a given coil orientation (fig. 7). Consequently, conductivities measured at different coil separations and

orientations can be used to infer conductivity changes with depth beneath a site (McNeill, 1980a, b) if lateral conductivity variations are small. The horizontal dipole orientation has a shallower exploration depth than the vertical dipole orientation for the same coil separation. Moreover, conductivities obtained from the horizontal dipole orientation are nearsurface weighted; for a given exploration depth, the response is largely governed by the conductivity of the uppermost third of the exploration depth. The vertical dipole orientation has a deeper exploration depth and is more center-weighted. Conductivities obtained in the vertical dipole mode are mostly affected by the conductivity of the middle third of the exploration depth.

Modeling conductivity distributions involved screening field results to eliminate unrealistic data; for example, where horizontal and vertical dipole data gave inconsistent trends. EMIX34 Plus, a computer program by Interpex Ltd., was used to process and interpret the data. Horizontal and vertical dipole conductivities for each station along a line were entered in the program, a starting conductivity model (consisting of layer thicknesses and conductivities) was entered that qualitatively fit the observed data, and then the computer displayed both the observed conductivities and conductivities calculated from the chosen model. The model was then adjusted to better fit the observed data. After reasonable agreement was obtained manually, the program was directed to adjust layer thicknesses and conductivities to obtain the best statistical fit.

Plan-view maps of the geophysical data were contoured manually, then the contours were digitized for preparing the illustrations in this report. Because the most highly conductive zone in the Fox Vacuum site is elongate

with a north-oriented strike, manual contouring was weighted in favor of the north-south transect data (lines A to F, fig. 6). As discussed later, west-east lines H, I, and J show a shift in the location of maximum conductivity interpreted to be an artifact of the position of transmitter and receiver coils during the survey. These west-east surveys, therefore, were largely ignored in the manual contouring of data.

# Core Sampling

Subsurface core was collected at three locations (locations 28, 29, and 30 in figure 3). A CME-75 drilling rig was used to auger three bore holes and to collect core with a wireline split-spoon core tube. Drilling locations were selected on the basis of preliminary geophysical survey results, discussed between BEG and the RRC Special Response Team on August 11, 1995. Bore hole BEG-1 (location 28) was augered in the driveway of the Buna Yard. BEG-2 (no. 29) was located on the edge of the barren ground in the adjacent pasture west of the yard, at the intersection of geophysical lines C and I (fig. 6). BEG-3 (no. 30) was located in a background area at the intersection of geophysical lines A and J (fig. 6), well away from site disturbance.

As previously stated, the depth to which acid had migrated was unknown and was a principal concern at the start of the investigation. Accordingly, exploratory bore holes were planned to go to a depth of approximately 30 ft (9.1 m), which is above the base of the Montgomery Formation in the vicinity of the Fox Vacuum site. BEG-1 was 32.4-ft (9.9-m) deep, BEG-2 was approximately 28-ft (8.5-m) deep, and BEG-3 was approximately 15-ft (4.6-m) deep. The depth of BEG-3 was stipulated on the basis of preliminary field measurements of pH on 1:1 water:soil extracts from samples taken at 1-ft spacings from the BEG-1 core. The contaminant

appeared to be contained entirely within the top 15 ft (4.6 m) of the subsurface; background readings were already found at a depth of 15 ft (4.6 m) in the contaminated area. These preliminary findings were later confirmed by more extensive laboratory analyses.

#### Pit Sampling

The 1976 aerial photograph clearly shows pits 1, 2, 3, 6, and 7 to be excavated. Development of pits 4 and 5 is not equally obvious.

We collected three cores at each of the seven (7) pits on site. Pits 1 and 5 did not appear to contain drilling or other oil-field materials, although pit 1 did contain household trash. The ground surface of pit 1 was overgrown by shrubs and trees, and soil was heavily rooted. This was opposite to expectation based on the aerial photograph. Pits 2, 3, 4, 6 and 7 each contained what appears to be crude-oil contaminated drilling mud. Each pit locally contained in excess of 7 ft (2.1 m) of waste material. The upper surface of these pit materials was crusted. We hypothesize that the crust formed in response to weathering, biological activity, seasonal wetting and drying, and compaction. Beneath the crust the pit materials appear to be made up of oil contaminated and water-wet, expanded bentonite with extremely high porosity and low mechanical strength.

Samples of the contaminated material in pits 2, 3, 4, and 6 were collected using a 6-ft-long (1.8-m-) tube with a piston to hold the sample in place. Other samples from the pits were collected using a shovel and hand-held bucket auger. These tools were cleaned between use in different pits.

The approximate dimensions and thickness of the pit materials were noted, although final estimates of pit area were more accurately determined from the 1976 aerial photographs.

# Water Sampling

A water sample was collected from a shallow well located 350 ft (106.8 m) east of the Fox Vacuum site (no. 1 in fig. 4). The large-diameter well (no. 1 in table 2) at the private residence had approximately 300 gallons (1135 L) of water in storage prior to sampling. The well was not purged, nor were multiple well-bore volumes of water discharged prior to sample collection. The water sample, therefore, was representative of the water being piped into the house for consumption but might be somewhat modified by biochemical reactions within the well bore relative to water composition in the formation outside of the well bore.

Three aliquots were collected. Waters to be analyzed for major and minor cations and anions were filtered through 0.45-µm cartridge filters. Waters to be analyzed for major and minor cations were acidified in the field with 6N HNO<sub>3</sub>; waters to be analyzed for anions were collected without treatment. Sample bottles were sealed with laboratory parafilm and kept cool during storage and delivery to the laboratory. Prior to collection of the sample for total coliform bacteria, the wellhead spigot was doused with isopropyl alcohol and then the tap was allowed to run for several minutes. Temperature was measured in the water streaming from the tap, and pH was measured in a sample immediately after collection. Ground-water samples were stored in the laboratory at 39.2°F (4°C) before analysis.

#### Well Plugging and Site Cleanup

After drilling was completed, we refilled the bore holes with a bentonitic cement grout, leaving a plug of native material taken from the auger flights at the top of the bore holes. We moved approximately 1/2 cubic yard of excess auger-flight cuttings from the BEG-2 and BEG-3 bore holes to

the Buna Yard site pad for temporary storage. Prior to leaving the site, dirt was removed from the drill rig, which then was cleaned using a steamcleaning unit. The few gallons of excess water were allowed to soak into the ground on the site pad or evaporate.

#### Storage and Archiving of Samples

Core from the three bore holes, BEG-1, BEG-2, and BEG-3, was packaged and labeled at the site and returned to the BEG laboratory in Austin, Texas, for further analyses. Pit sediment samples in plastic tubes or sample bags were stored in an enclosed truck until delivery to BEG laboratory. Samples then were stored at constant laboratory conditions until they were subsampled and composited. Pit sediment composites and archived (leftover) portions were stored at 39.2°F (4°C).

# Compositing of Pit Samples

The pit sediment samples were, in most cases, collected and stored in clear polycarbonate plastic tubing (3-inch [76-mm] diameter) and sealed with polyethylene caps and tape. These cores were split and sampled in the laboratory. A subsample representing a smaller vertical sample of each core was removed and placed into glass jars and mechanically blended. Some samples were collected and stored in plastic bags. For these samples, the total sample was blended by hand prior to subsampling into glass jars and blending. The three cores from each pit were composited to make one sample per pit by combining equal masses and blending. The resulting composited samples were then subsampled for the various laboratory analyses.
#### Analyses

pH, EC, and Sulfate Measurements in Core Samples

These measurements were performed on 1:1 extractions prepared both in the field and at the BEG laboratory. Sample material was removed from the core at 1-ft (0.3-m) intervals. For core BEG-1, all samples were collected prior to the core being packaged at the site. A mass of ~30 g of soil was weighed and mixed with a calculated mass of deionized water (determined by estimating the water content of the sample) to achieve a 1:1 mixture of dry sample:total water. In the field the samples were repeatedly shaken then allowed to settle. A combination glass electrode and portable pH meter were used to measure pH. For BEG-2, three samples were prepared in the field. Upon return to the laboratory, both BEG-2 and BEG-3 cores were sampled at 1-ft (0.3-m) intervals. In the laboratory, samples were mechanically shaken for 1 hr then centrifuged to obtain a particle-free liquid. The samples prepared in the laboratory were remeasured for pH using a combination ion-selective electrode and portable pH meter. Electrical conductivity (EC), which indicates the quantity of soluble salts in an aqueous sample, was determined on the supernatant using a direct-readout micro-conductivity cell and corrected to 77 °F (25 °C). Sulfate concentrations of all extractions were determined by ion chromatography.

### Water Extractable Anions in Pit Sediments

Pit sediments were composited in the laboratory for analysis of waterextractable anions, total metals, total petroleum hydrocarbons, leachable metals, and volatile and semivolatile organics. Analyses were performed by RRC Surface Mining and Reclamation Division Laboratory, the BEG Mineral Studies Laboratory, and Chemsolve, Inc., Austin, Texas.

Sediment samples from the disposal pits were oven dried prior to analysis. Moisture-free samples were then extracted with water on a mechanical shaker for 1 hr. The resulting slurries were centrifuged and filtered to produce particle-free solutions. An aliquot of each solution was then treated with hydrogen peroxide to remove the bulk of the organics present. The resulting solutions were analyzed for chloride, bromide, nitrate, phosphate, and sulfate by ion chromatography. Fluoride could not be measured because of interference from residual organic compounds. The result for each anion was then expressed as mg/kg on a moisture-free basis.

# Total Metals in Pit Sediments

The oven-dried sediments were subjected to two dissolution techniques. A fusion technique (with lithium borate) provides the solution for which silicon and barium are quantitatively measured by inductively coupled plasma-optical emission spectrometry (ICP-OES). The second technique involves a mixture of concentrated nitric, perchloric, hydrofluoric, and hydrochloric acids, which completely dissolves all but a few very resistant minerals (such as barite). The resulting solutions are also quantitatively analyzed by ICP-OES for metals.

### TCLP Metals in Core and Pit Sediments

Core from bore holes BEG-1, BEG-2, and BEG-3 and composited samples from all 7 pit areas were analyzed for leachable metals. The toxicity characterization leaching procedure (TCLP), as outlined in EPA method 1311, is intended to measure the solubility (mobility) of metals in a landfill. Eight metals are regulated by the TCLP: arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver. A waste (soil) sample (20 g) is extracted with an amount of extraction fluid (400 mL) equal to 20 times the weight of the

waste sample. The extraction fluid is an acetic acid solution at pH 4.93 or pH 2.88, dependent on the alkalinity of the sample. The resultant mixture is placed in a plastic bottle and rotated end-over-end at 30 rpm for 18 hr at room temperature (73 °F [23 °C]). The liquid extract is separated from the solids by filtration through a 0.6- to 0.8-micron glass fiber filter. The filtrate is analyzed by ICP-OES, except mercury, which is done by mercury analyzer (cold vapor atomic absorption).

### Organic Content of Pit Sediments

TPH was determined by gravimetric techniques in a two step process. First oil and grease is determined by method 5520E (American Public Health Association, 1992). On the residue so obtained TPH is determined by method 5520E. For oil and grease, less than 3 g of sample is extracted in 230 mL of a 80:20 mixture of hexane and methyl tert-butyl ether (MTBE). The mixture is placed in a thimble filter and extracted in a Soxhlet apparatus for 4 hr. The recovered solvent is distilled in a water bath at 70 °C (158 °F). The residue is weighed and by definition is oil and grease. However, it includes any material recovered as a substance soluble in the solvent such as other organics, sulfur compounds, and chlorophyll. No known solvent will selectively dissolve only oil and grease.

The oil-and-grease residue, 3 g of silica gel, and 100 mL of the 80:20 solvent is stirred and poured through a chromatography column to filter residue and solvent. The recovered solvent is distilled in a water bath at 70 °C (158 °F). The residue is weighed and by definition is TPH. The materials not eliminated by silica gel adsorption are designated hydrocarbons by this test. Silica gel has the ability to adsorb polar compounds and consequently fatty

acids are selectively removed from solution. The more polar hydrocarbons such as complex aromatic compounds may also be adsorbed by the silica gel.

The gravimetric technique is a useful screening step for determining the presence and level of hydrocarbon contamination and provides good results on fresh material. However, because the method reports biomass as TPH, the method demonstrates little or no decrease in hydrocarbon content as the result of bioremediation. Thus, its use is not recommended for setting cleanup standards, monitoring decrease in soil oil content as treatment progresses, or certifying that remediation is complete (Deuel and Holliday, 1994; Troy and others, 1994). In this case, gas chromatography (GC) with flame ionization detection (FID) is the method of choice (EPA modified method 8015).

Benzene, toluene, ethylbenzene, and xylene (BTEX) were determined by EPA method 8020, a purge and trap technique. The waste sample is extracted in methanol. Helium is bubbled through the methanol mixture to purge the BTEX components followed by trapping on a "charcoal" column. The trap is heated to expel the BTEX. Identification is by capillary gas chromatography with photoionization detector followed by mass spectrometry for confirmation.

Semivolatile organics were determined by gas chromatography-mass spectrometry (GC-MS) according to EPA method 8270, a capillary column technique. The method quantifies most neutral, acidic, and basic organic compounds that are soluble in methylene chloride at molecular weights of less than 500 or carbon number of 40 or less. Capillary gas chromatography is used to separate compounds in the extract for their qualitative and quantitative analysis by mass spectrometry. The capillary column (30 m x 0.21

mm ID) is directly coupled to the source mass spectrometer, which is computer controlled. For soil samples, the estimated quantitation limit for determining an individual compound is about 1 mg/kg (wet weight).

### Ground-Water Ionic Composition

Cations were determined using ICP-OES. Fluoride, chloride, bromide, nitrate, phosphate, and sulfate anions were determined by ion chromatography. Bicarbonate was determined by titration.

Bacterial analysis of the sample of ground water was conducted by the Sabine River Authority in Beaumont, Texas, following the membrane filter method (method 909A, American Public Health Association, 1989). The total coliform test is considered a reliable indicator of the possible presence of fecal contamination and consequently a correlation with pathogen.

#### RESULTS

#### Soil Texture and Water Content

Soil texture observed in the three cores at Fox Vacuum site (samples 28, 29, and 30, fig. 3) is consistent with the description of sand clay loams of the Kirbyville-Waller association (Neitsch, 1982). Very-fine-grained sand in a muddy matrix extends to a depth of 12 to 13 ft (3.7 to 3.9 m) at the site (fig. 8). Soil-forming processes have depleted the clay content in the uppermost 1.5 to 1.7 ft (0.46 to 0.52 m). Fractures record past episodes of wetting and drying in the soil. Beneath the surficial clayey sand is a thick clay interrupted at several depths by thin (less than 0.5-ft [0.15-m] thick) muddy sand stringers.

Soil in three auger holes (24, 25, and 26, fig. 3) was water saturated at depths of 1.5 to 2.6 ft (0.46 to 0.79 m) in April 1995, which also is consistent



Figure 8. Soil texture observed in core at the Fox Vacuum site. (a) BEG-1 in the Buna Yard driveway, (b) BEG-2 at the edge of the barren ground, (c) BEG-3 in an uncontaminated background location. Texture shown is maximum grain size (VF–very fine sand). See figure 2 for locations of bore holes numbered 28, 29, and 30, respectively.

with the description of the Kirbyville-Waller association (Neitsch, 1982). The soil was not saturated in August 1995. Depth to water in the BEG-1 bore hole was measured at 24.6 ft (7.5 m). Although water level might not have fully recovered from the augering of the bore hole before the measurement was taken, it is clear that soil-water content was much decreased from its saturated level near ground surface during the earlier Spring months.

# pH, SO<sub>4</sub>, and Conductivity Data

Samples numbered 23 to 27 (fig. 3) were collected in April 1995 using a hand auger. Depth of the five auger holes ranged from 2.2 to 3.6 ft (0.67 to 1.1 m). Water was extracted from three of the five auger holes (24, 25, and 26, fig. 3) using tygon tubing attached to a 50-cm<sup>3</sup> syringe.

In the samples collected in the Buna Yard driveway, pH of the soilwater slurry was consistently low (pH between 1.7 and 3.7). The pH of water siphoned from the three auger holes also was between 1 and 3. These data are consistent with earlier measurements of pH, sulfate, and conductivity in soil samples 1 to 14 (fig. 3), in which the lowest pH was 1.0 and the highest sulfate concentration was 16,253 mg/L (table 1). Samples collected along the ditch on the north side of Alvarez Road (21 and 22, fig. 3) also show evidence of contamination. Samples 21 and 22 have sulfate concentrations of 248 and 868 mg/L and electrical conductivities of 57 and 150 mS/m (table 1), respectively, which are above background. Average dissolved sulfate in local ground water is 2.7 mg/L and average electrical conductivity of ground water is 20 (10<sup>1.3</sup>) mS/m.

BEG-1 (28, fig. 3) in the Buna Yard driveway yielded extreme values of pH, sulfate, and electrical conductivity among core data from the three deeper

later.

bore holes collected in August 1995 (fig. 9). Samples from the uppermost 4 ft (1.2 m) of core in all three settings (driveway, barren ground, background) yielded elevated ph, sulfate, and electrical conductivity; this section is designated zone 1. At depths greater than 9 to 10 ft (2.7 to 3.0 m), pH, sulfate, and electrical conductivity were near background in all three cores (fig. 9). Between depths of 4 to 9 ft (1.2 to 2.7 m), pH, sulfate, and electrical conductivity grade from the extreme values in the main zone of contamination to their background values. This intermediate section is designated zone 2 (fig. 9). The pH values of samples at depths greater than 10 ft (3.0 m) are slightly acidic (fig. 8a), typical of the pH of the Kirbyville-Waller soil association (Neitsch, 1982).

Ground water bailed from bore hole BEG-1 (28, fig. 3) had a pH of 5.47, sulfate of 361 mg/L, and electrical conductivity (EC) of 98 mS/m (table 3). Sulfate and conductivity in this water sample are above background whereas pH is slightly less than background (fig. 9).

Table 4 presents the TCLP metals, oil and grease, and total petroleum hydrocarbons in the three cores. It is useful to note that barium content in the "background" sample (map no. 30, BEG-3) covers the same range as that beneath the site pad (map no. 28, BEG-1). The "background" sample is also notable for comparison with samples from the drilling-mud pits, discussed later.

### Pit Data

The earthen pits at the Fox Vacuum site contain spent drilling muds contaminated by crude oil and formation water encountered during drilling. Crude oil and formation water generally are the chief contaminants of



Figure 9. Distribution of pH, sulfate, and electrical conductivity determined in saturation-paste extracts from core at the Fox Vacuum site. Zone 1 is interpreted to be the interval containing the source of contamination in the Buna Yard driveway. Zone 2 is interpreted as a transition from contaminated to largely unaffected ground.

Table 3. Composition of ground-water samples. See figure 4 for location of well no. 1 and figure 3 (sample 28) for location of BEG-1. All ionic concentrations in mg/L.

Name	рН	Sodium	Potassium	Magnesium	Calcium		
Well no 1	5 99	87	0.3	О З	2 57		
BEG-1	5 47	135	1.6	21.5	30.9		
62-25-102	nr	21	nr	4	10		
62-25-307	nr	30	nr	3	16		
62-25-802	nr	41	nr	3	14		
MSL no.	Chloride	Sulfate	HCO3	CO3	Fluoride	Bromide	Nitrate
95-306A	9.1	0.78	15.4	nd	*0.5	*0.1	1.39
95-307A	44.8	361	7.5	nd	0.68	1.3	*0.1
62-25-102	17	5	61	nr	nr	nr	10
62-25-307	20	2	79	nr	nr	nr	27
62-25-802	40	7	55	nr	nr	nr	34
MSL no.	Iron	Barium	Strontium	Aluminum	SiO <sub>2</sub>		
95-306A	0.02	0.02	0.01	0.03	20.9		
95-307A	0.56	0.30	0.38	0.87	67.8		
62-25-102	nr	nr	nr	nr	nr		
62-25-307	nr	nr	nr	nr	nr		
62-25-802	nr	nr	nr	nr	nr		
					,		
	EC	TDS	Charge	Facies			
MSL no.	(mS/m)	(mg/L)	balance (%)	type			
95-306A	6.16	60.1	-0.7	Na-HCO3			
95-307A	97.75	674.3	1.8	Na-SO <sub>4</sub>			
62-25-102	nr	128	-0.04	Na-HCO3			
62-25-307	nr	177	0.35	Na-HCO3			
62-25-802	nr	194	0.17	Na-HCO3			

\* near detection limit

nd not detected

nr not reported

Table 4. TCLP and total organic content analyses on core samples from the acid-contaminated (bore holes 1 and 2) and background (bore hole 3) areas. Map number refers to sample locations shown in figure 3.

Map no.		28	28	28	29	29	29	30	30	30
Bore hole no.		1	1	. 1	2	2	2	3	3	3
Depth (ft)		3	9	16.5	3	9	16.5	3	9	16.5
Date collected	Unit <b>s</b>	8/15/95	8/15/95	8/15/95	8/16/95	8/16/95	8/16/95	8/16/95	8/16/95	8/16/95
Arsenic	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Barium	mg/L	0.17	0.43	1.7	0.27	2.7	2.2	0.54	1.2	1.8
Cadmium	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Chromium	mg/L	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Lead	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Mercury	mg/L	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002
Selenium	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Silver	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Oil and grease	weight %	0.01	0.20	0.24	0.20	0.12	0.19	0.06	0.07	0.06
Total petroleum	weight %	0.01	0.03	0.0	0.19	0.0	0.10	0.00	0.01	0.00

drilling muds (Deuel and Holliday, 1994). Volume of the waste material, concentration of contaminants, and concentration thresholds defined as action levels by regulatory authorities are the principal considerations for evaluating risk to health and safety and remediation alternatives.

Waste materials in the pits at the Fox Vacuum site make up a volume of almost 118,000 ft<sup>3</sup>, or 2.7 acre-ft (3,340 m<sup>3</sup>) (table 5). Pit size was estimated on the basis of both ground-based measurements and examination of the 1976 aerial photograph; depth was extrapolated from probes of sediment thickness. Pits 1 to 4 and 6 were assumed to have the shape of an oblate ellipsoid, which reasonably fits the measured profile of the side of several pits. Pit 1 was assumed to contain waste material similar to that in pits 2, 3, 4, 6, and 7 on the basis of evidence of a 1976 aerial photograph. Pit 5 was assumed to be undeveloped (not excavated). Pit 7 and the channel from pit 4 to pit 7 were assumed to have a triangular cross section. An estimate of minimum fluid content comes from weight loss at 221 °F (105 °C) in sample processing for oilcontaminated muds. Weight loss averaged 42 percent, which includes loss of moisture and volatile organic carbons but not of liquid hydrocarbons.

Chloride content varies among the composited sediment samples from the pits (table 6). Oil-contaminated mud from pit 4 (98.4 mg/kg) has only onefifth the chloride content of waste in pits 2, 3, 6, and 7 (average of 555 mg/kg). Chloride is lowest in uncontaminated soil samples from pits 1 and 5, yet the 93 mg/kg value for pit 1 is above background. As previously stated, spent drilling muds might be present beneath the soil samples collected at pit 1. In all samples chloride is less than the 3,000 mg/L concentration limit for disposal of low-chloride drilling fluid by land farming without a permit (Rule

Table 5. Estimates of volume of pit contents at Fox Vacuum site

Pit	Assumed maximum depth (ft)	Radius (ft)	Area (ft <sup>2</sup> )	Wet volume (ft <sup>3</sup> )	Assumed shape
1	5	10	340	1.133	Oblate ellipsoid
2	9	17	873	5,236	Oblate ellipsoid
3	10	21	1,364	9,090	Oblate ellipsoid
. <b>4</b> 🖉	9	17	873	5,236	Oblate ellipsoid
5	0	17	873	0	Not excavated
6	9	17	873	5,236	Oblate ellipsoid
7	9	na	20,330	91,493	Tetrahedron
Channel	5	na	844	1,688	Tetrahedron

Total

117,424

Pit contents assumed to be 50 percent water by volume
na radius not applicable; area of pit 7 based on two isoceles triangles 124-ft base x
256-ft sides and 72-ft base x 124-ft sides; area of channel based on one isoceles
triangle 5-ft base x 338-ft sides.

Table 6. Summary of water-extractable anions and total metals in disposal-pit samples from the Fox Vacuum site. Three samples taken in 6-ft- (1.8-m-) long tubes and composited for each pit. Analytical unit is mg/kg. Map numbers refer to sample locations shown in figure 3.

Map no.	31	32	33	34	35	36	37	
Pit no.	1	2	3	4	5	6	7	
MSL ID no.	95-267	95-273	95-279	95-288	95-292	95-297	95-299	
Date collected	8/16/95	8/16/95	8/16/95	8/17/95	8/17/95	8/17/95	8/17/95	
Water-extractable anions								
Chloride	93.3	598	439	98.4	23.6	618	565	
Nitrate	*1.6	2.9	*0.3	*0.8	3.0	*0.4	*1.1	
Phosphate	*3.9	34.9	12.1	nd	nd	15.1	5.8	
Sulfate	1140	1600	1170	1660	678	1790	912	
			<u>Total m</u>	<u>ietals</u>				
Barium	294900	61900	92000	202200	1300	93900	104600	
Calcium	16380	28350	14670	25200	347	16340	19780	
Sodium	1770	9000	5300	4820	684	7260	5320	
Potassium	3060	11310	7290	5120	752	9340	9180	
Magnesium	2550	6800	3900	3980	523	4870	6380	
Aluminum	17300	55800	41260	29860	18470	46360	56450	
Silica	173000	518000	572000	279000	870000	551000	473500	
Iron	18090	27960	25750	25660	23650	24070	30730	
Titanium	816	2540	2200	1350	2320	2200	2730	
Cobalt	22	29	28	27	21	28	29	
Chromium	255	433	276	179	38	219	450	
Copper	36	14	29	20	*10	24	22	
Manganese	502	274	378	366	39	319	237	
Nickel	<14	21	23	17	<14	17	22	
Molybdenum	<10	<10	<10	<10	<10	<10	<10	
Zinc	333	177	498	381	10	426	289	
Arsenic	<60	<60	<60	<60	<60	<60	<60	
Cadmium	~ 2	~2	~2	2	~2	*2.2	~2	
Vanadium	24	72	54	39	55	55	75	
Lead	341	106	346	426	*26	243	178	
Antimony	<160	<160	<160	<160	<160	<160	<160	
Selenium	<138	<138	<138	<138	<138	<138	<138	
Tin	<18	<18	<18	<18	<18	214	<18	
Lithium	<8	28	17	<8>	<8	18	27	
Beryllium	1.1	2.4	1.9	1.8	1.5	2.3	2.6	
Strontium	3750	869	945	1510	31.1	947	882	
Zirconium	32.5	91.7	74.6	37.7	47.5	79.5	90.6	
Uranium	<500	<500	<500	<500	<500	<500	<500	
Thorium	<76	<76	<76	<76	<76	<76	<76	
Phosphorus	342	480	378	396	*91	489	446	
Cerium	<110	<110	<110	<110	<110	<110	<110	
Lanthanum	16.6	34.8	28.3	22.9	24.5	34.0	35.8	
Rubidium	~1000	~1000	~1000	~1000	~1000	<1000	<1000	

< less than indicated value

reported value near detection limit

nd not determined

8, Railroad Commission of Texas, 1994), assuming reasonable values of porosity (42 percent) and bulk density (<12.5 lb/gal, <1,500 kg/m<sup>3</sup>).

TCLP metals (table 7) are all well under EPA regulatory limits. Only barium exceeds 1 mg/L, ranging from 1.4 to 8.8 mg/L, excluding the sample from pit 5. The TCLP barium content determined in core from BEG-3 in the unaffected area (the "background" sample) ranges from 0.54 to 1.8 mg/L (table 4). Composited samples from pits 3 and 4 are within this range; only samples from pits 1, 2, 6, and 7 exceed the background value. Nonetheless, barium's regulatory TCLP limit is 100 mg/L. Barium is commonly added to drilling mud in the form of finely ground barite (BaSO4) to increase the weight of the mud. The high value of barium in the pit-1 sample supports the expectation that spent drilling mud lies beneath the surficial soil in that area. High totalmetal contents of calcium, sodium, potassium, magnesium, aluminum and silica (table 6) are expected because the drilling mud is made up of silicatebased clay minerals.

Volatile aromatic hydrocarbons, including benzene, ethylbenzene, xylene, and toluene, were found at only low concentrations in the spent drilling mud (table 7). Benzene, toluene, ethylbenzene, and xylene and total petroleum hydrocarbons (TPH) were highest in pit 4. Total BTEX in the drilling mud also was highest in pit 4 (12.5 mg/kg). TPH in all composited samples, however, is less than 1 percent, the cutoff value for oilcontaminated soil requiring excavation for remediation or disposal (Rule 91, Railroad Commission of Texas, 1994). Benzene concentration is less than that of xylene and toluene, which is typical of crude oil (Nyer, 1993). The ratios of volatile constituents are generally similar among the samples; ethylbenzene/toluene is the most variable ratio. The content of methyl

Table 7. Total organic content, BTEX compounds, and TCLP metals in disposal-pit samples from the Fox Vacuum site. Map numbers refer to figure 3.

Map no.		31	32	33	34	35	36	37
Pit no.		1	2	3	4	5	6	7
MSL ID no.	. •	95-267	95-273	95-279	95-288	95-292	95-297	95-299
Date collected	Units	8/16/95	8/16/95	8/16/95	8/17/95	8/17/95	8/17/95	8/17/95
			I	otal organics				
Oil and grease	weight %	0.50	0.60	0.65	2.5	0.03	0.54	0.81
Total petroleum hydrocarbons	weight %	0.12	0.19	0.18	0.92	0.02	0.18	0.49
			BTE	EX compounds	<b>i</b> .			
Benzene	μg/kg	na	150	<50	300	na	ත්0	<50
Toluene	μg/kg	na	250	50	2200	na	200	<50
Ethylbenzene	μg/kg	na	1200	⊲50	1700	na	ත්0	<50
o-Xylene	μg/kg	na	1600	100	2300	na	300	<50
<i>m,p</i> -Xylenes	μg/kg	na	3700	150	6000	na	350	<50
MTBE	μg/kg	na	<500	<500	<500	na	<b>ح500</b>	<500
Total BTEX	μg/kg	-	6,900	<400	12,500	-	<950	<250
			ц	CLP leachate		٥		
Arsenic	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Barium	mg/L	5.	4.5	1.6	1.4	0.19	2.1	8.8
Cadmium	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Chromium	mg/L	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Lead	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Mercury	mg/L	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002
Selenium	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Silver	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
· •								

near detection limit

nd not detected

na not analyzed

tetrabutyl ether (MBTE), a gasoline additive, is below the detection limit, which is consistent with the contaminant having a crude-oil source.

Semivolatile organic compounds (table 8) are dominated by polycyclic aromatic hydrocarbons (PAH). PAH concentrations are all low, which is consistent with the low total TPH (table 7). The PAH's with the highest concentration are methyl naphthalene (8.1 mg/kg) and naphthalene (5.7 mg/kg), which are simple PAH compounds. Other PAH's with detectable concentrations (>1 mg/kg) are anthracene, chrysene, dibenzofuran, fluoranthene, phenanthrene, and pyrene. These findings are again consistent with the contaminant having a crude-oil source.

### Ground-Conductivity Survey Results

Electrical conductivities ranged from nearly 175 mS/m beneath the site pad, 50 to 75 mS/m in the barren zone, to <50 mS/m in the undisturbed pasture (fig. 10). Readings adjacent to the pits were higher than background levels but lower than readings on the site pad.

### **Background Areas**

To understand which ground-conductivity values are anomalous at the site, it is necessary to establish the background conductivity. Geologic materials have a natural electrical conductivity that is related to pore volume, pore shape, moisture content, pore fluid chemistry, and permeability. At the Fox site, an electrical conductor (sulfuric acid) has infiltrated the pore space of the near-surface sediments, which changes the pore fluid chemistry and increases its conductivity.

East-west lines H, I, and J extend westward from the area of obvious surface contamination and show lower ground conductivities along the

Table 8. Semivolatile organics in pit sediments at the Fox Vacuum site determined by GC-MS using EPA procedure 8270. Analyzed sample was composite of material from pits 2, 3, 4, 6, and 7. Units are mg/kg and practical quantification limit is 1.0 mg/kg for all analyses.

	Pit
Organic compound	composite
2.4 dimethylphenol	<1.0
2-methylnaphthalene	8.1
3&4-methylphenol	<1.0
Acenaphthylene	<1.0
Anthracene	1.6
Benzo(a)anthracene	<1.0
Benzo(a)pyrene	<1.0
bis(2-ethylhexyl)phthalate	<1.0
Chrysene	3.1
Dibenzofuran	1.1
Fluoranthene	2.2
Naphthalene	5.7
Phenanthrene	1.2
Pyrene	<1.0

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Figure 10. Apparent conductivity measured in the horizontal dipole mode at 10-, 20-, and 40-m coil separations along transects at the Fox Vacuum site. Plotted versus distance from the northern (A to G) ends of the survey lines. See figure 6 for location of survey lines.



western part of each line for both horizontal (fig. 10) and vertical dipole electromagnetic data. Background conductivity values of 25 to <50 mS/m (horizontal dipole mode) are reached west of the intersection of these lines with line B (fig. 6). Vertical dipole values are similar to horizontal dipole values except along line K, where power line noise has artificially increased vertical dipole values for the longer (20-m and 40-m) coil separations.

Along the north-south lines, background conductivity values of 25 to 50 mS/m in the horizontal dipole mode are reached along all of lines A and B, part of line D northward of a point about 98.4 ft (30 m) north of its intersection with line H, and at the northern end of line F (fig. 10). Conductivity values along line G, located at the east boundary of the property, approach background at the north end of the line but appear to be generally higher than background values found in the western and northern parts of the site.

Analysis of apparent conductivities for multiple coil separations in background areas shows that conductivities do not vary greatly with depth in these areas. Along line A, for example, horizontal dipole conductivities are nearly identical at about 40 mS/m for the 10-m and 20-m coil separations and fall to 31 to 37 mS/m for the 40-m separation (fig. 10). This suggests that conductivities are relatively low throughout the upper few meters of the subsurface and that ground conductivity decreases with depth. Vertical dipole data are more susceptible to noise and are more erratic than horizontal dipole data along line A. Nevertheless, vertical dipole values are in the same range as the horizontal dipole values (generally 30 to 45 mS/m for the 10-m and 20m separations). Vertical dipole data also have lower conductivities for longer

coil separations, which further suggests that conductivity decreases with depth in the upper 20 or 30 m.

Simple three-layer conductivity models for the "background areas" were constructed to fit electromagnetic data generated for the three coil separations and two coil orientations. Good fits were obtained with models having a thin, poorly conductive surface layer underlain by a thicker, more conductive layer, which is in turn underlain by a poorly conductive layer to the deepest depth investigated. These layers match very well the hydrogeologic conditions in the vicinity of the site, as discussed next.

Computed surface layer conductivities ranged from less than 0.5 mS/m to 18 mS/m for thicknesses of 5.6 to 15 ft (1.7 to 4.6 m). This surface layer probably represents relatively nonconductive material that is not water saturated. This matches the depth to the water table at a shallow well (no. 1, fig. 4) east of the Fox Vacuum site (13.1 ft [4.0 m]) measured during the week of the geophysical survey.

Below this is a layer characterized by higher modeled conductivities of 64 to 102 mS/m and thicknesses of 36 to 95 ft (11 to 29 m). This layer probably represents a water-saturated, relatively clay-rich geologic unit and matches the estimated thickness of the Montgomery Formation in the vicinity of the Fox Vacuum site (fig. 5). Below this is another relatively nonconductive layer with a modeled conductivity of 2 to 31 mS/m. This layer reflects a watersaturated geologic unit that contains less clay than the layer above it, such as the main part of the Chicot aquifer.

Laboratory analyses of samples acquired from bore hole BEG-3 (no. 30, fig. 3), located at the intersection of lines A and J (fig. 6), show sulfate content dropping to below detection limit by depth of 4 ft (1.2 m) and soil water

electrical conductivities that are somewhat higher above 4 ft (1.2 m) and below 11 ft (3.4 m) than they are between these depths (fig. 9). Relatively low conductivities between depths of 4 and 11 ft (1.2 and 3.4 m) in BEG-3 agree with those modeled for layer 1 from the electromagnetic data, and higher conductivities below 11 ft (3.4 m) in BEG-3 appear to be modeled by layer 2 in the electromagnetic data. The electromagnetic model for layer 1 does not subdivide the somewhat higher conductivities measured in the upper 4 ft (1.2 m) of BEG-3 from those measured between depths of 4 and 11 ft (1.2 and 3.4 m). The deepest relatively nonconductive layer was not reached by the BEG-3 boring.

### Highly Conductive Areas

East-west lines H, I, and J and north-south lines C, D, E, and F (fig. 6) each cross an area that has markedly higher ground conductivities than the surrounding area and that coincides with the Buna Yard driveway. Plan-view maps of conductivity show an area of high conductivity that is elongate in a northwesterly direction (figs. 11, 12, and 13) and has two conductivity peaks that are best illustrated on lines E and F (fig. 10). Apparent ground conductivity increases from background values of between 25 and 50 mS/m to nearly 175 mS/m at the northern peak and about 160 mS/m at the southern peak for the 10-m horizontal dipole coil configuration (lines E and F, fig. 10). Each peak is about 82 ft (25 m) in width.

Above-background conductivities extend about 262 ft (80 m) northsouth and as much as 262 ft (80 m) east-west, although conductivity values above 75 mS/m are found over an east-west distance of 100 ft (30.5 m) or less (fig. 11). Intermediate conductivities extend east, west, and southwest of the highest conductivity zone. Background values are not reached until 131.2 ft



Figure 11. Distribution of ground conductivity interpreted from surveys with 10-m coil separation.



Figure 12. Distribution of ground conductivity interpreted from surveys with 20-m coil separation.



(40 m) west of the peaks on lines H, I, and J. East of the Buna Yard driveway, only line H appears to reach background levels before the end of the line. Conductivities at the east end of line J and I did not reach the low background levels observed at the west end of the line. Slightly elevated conductivities (above 50 mS/m for horizontal dipole orientation and 10-m coil spacing) are found on line K along Alvarez Road southwest of the site entrance for a distance of about 115 ft (35 m), and along line G at the east boundary of the site for a distance of about 100 ft (30.5 m) (figs. 10 and 11).

Conductivity data collected at three coil separations show that the highly conductive material is found near the surface. Profiles with the highest horizontal dipole conductivities for the 10-m coil separation, lines F and I, both have apparent conductivities that decline rapidly with increasing coil separation. For line I, peak values decrease from 140 mS/m at the 10-m separation, to 80 mS/m at the 20-m separation, to near background at 50 mS/m for the 40-m separation (fig. 10). Because the horizontal dipole orientation is most sensitive to the upper third of its exploration depth (fig. 7), these results suggest that the highly conductive material extends no deeper than a few meters beneath the most conductive area, which is also indicated by the bore hole data (fig. 9). Vertical dipole conductivities (not shown) across the highly conductive zone actually become negative on some of the lines, particularly east-west lines I and H and north-south line F. These negative values imply both that conductivities are changing greatly over short lateral distances (the assumption of lateral continuity is violated) and that ground conductivities are high enough to cause a nonlinear response in the vertical dipole mode of the instrument.

Three-layer conductivity models were constructed along line I using horizontal and vertical dipole apparent conductivities for the three coil separations. A three-layer model provides a fair fit to the 10-m electromagnetic and geochemical data for the area with the highest observed conductivity. This model consists of a very thin (0.7 ft [0.2 m]), poorly conductive (14 mS/m) surface layer underlain by a thin (6.6 ft [2 m]), very conductive layer (690 mS/m). This layer in turn is underlain by a layer with modeled conductivity of less than 1 mS/m that extends to an unknown depth.

Bore hole BEG-1 (no. 28, fig. 3), located at the conductivity peak near the intersection of lines F and H (fig. 6), shows a contaminant profile well matched by the electromagnetic layered-model results. Sulfate concentration and electrical conductivity are highest in the upper 4 ft (1.2 m) of the borehole and lower but still above background to a depth of 10 ft (3 m). The modeled 6.6-ft (2-m) base of the very conductive layer most likely reflects a composite of zones 1 and 2 indicated in figure 6. It is likely that the thin, poorly conductive surface layer consists of contaminated but relatively dry material. Below a depth of 10 ft (3 m), electrical conductivity measured in the BEG-1 core differs little from that measured at similar depths in core from bore holes BEG-2 and BEG-3 (fig. 6), which is reflected in the basal model layer conductivity of less than 1 mS/m.

Profiles of ground conductivity in the horizontal dipole orientation also show that the conductivity peak appears to be shifted westward relative to the Buna Yard driveway. The lateral shift increases with increasing coil separation along lines H, I, and J (fig. 10). On line I, for example, the 10-m separation peak is near the intersection with line F, the 20-m separation peak

is about 50 ft (15.2 m) west between the intersections of line I with lines D and E, and the 40-m separation peak, though much diminished, is 32.8 ft (10 m) farther west near the intersection of lines I and C. Contoured values of ground conductivity beneath the barren ground and adjacent area with stressed vegetation mapped using only north-south transects, however, were also somewhat higher in the 20-m than in the 10-m surveys along north-south lines C, D, E, and F (compare figs. 11 and 12).

The apparent migration most likely is an artifact of having the transmitter coil east of the receiver coil on east-west lines during data acquisition (fig. 7a, b). Having the transmitting coil directly over a shallow conductive body may augment the primary field strength, cause an anomalously strong secondary field that is detected by the receiver coil, and contribute to the apparent western shift of ground-conductivity peaks with longer coil separations. An alternative interpretation, that conductive fluids have migrated westward and downward from the highly conductive area near ground surface, is not strongly supported by geochemical data from bore hole BEG-2, which shows the contaminant profile reaching background values at 2-ft (0.6-m) more shallow depth than in BEG-1 (fig. 9). Between depths of 16.4 to 19.7 ft (5 to 6 m), sulfate concentration and electrical conductivity appear a little higher and pH appears a little lower in core from both BEG-1 and BEG-2 (fig. 9). This would be consistent with the interpretation that conductive fluids moved westward and downward from the Buna Yard. The difference between BEG-1 and BEG-2 cores might be large enough to account for the increased ground conductivity in the 20-m survey.

Slightly elevated horizontal dipole conductivities observed along Alvarez Road southwest of the site entrance (line K, figs. 10 and 11) most

likely indicate elevated ground conductivity. The 10-m data along Alvarez Road probably show a real increase in ground conductivity because (a) the increase occurs only southwest of the site entrance, whereas the power line extends the entire length of line K, and (b) samples taken from cores in the drainage ditch along line K have low pH and elevated sulfate concentrations and electrical conductivities (no. 21 and 22, fig. 3, table 1). The 20-m and 40-m separation conductivities, however, are clearly affected by power line noise.

Conductivities also are above-background at the eastern end of lines J and I and along the southern part of line G (figs. 10 and 11). A plateau on the eastern flank of the main conductivity peak on line J is consistent with a secondary ground-conductivity peak located at the line of disposal pits between lines F and G. Elevated conductivities along line G are found near pits 2 and 3.

### Ground-Water Composition

Ground water at well no. 1 located 350 ft (106.8 m) east of the Fox Vacuum site (fig. 4) is drawn from the Montgomery Formation (see fig. 5). This water has total dissolved solids (TDS) of 60 mg/L and is a sodium– bicarbonate type water, that is, sodium and bicarbonate ions account for more than 50 percent of cation and anion electrical charge. Other ground waters from the Montgomery Formation in the vicinity of the Fox Vacuum site have TDS from 128 to 194 mg/L and are also the sodium–bicarbonate type (table 3). Well no. 1 had a fecal coliform concentration of 58 colonies/100 mL, which exceeds the U.S. Public Health Service standard of 1 colony/100 mL. Such a high coliform count is typical of large-diameter, "hand-dug" wells with a large standing water column that does not get repeatedly flushed or circulated. In other words, the total coliform might reflect a population of

bacteria living within the well bore or might reflect ground-water contamination (for example, from a septic tank). The fact that dissolved nitrate is low (table 3), however, suggests that contamination from a septic tank has not occurred, so that the bacteria population most likely is endemic to the well.

# INTERPRETATION

The potential contaminants of concern at the Fox Vacuum site are:

- sulfuric acid in the Buna Yard driveway and adjacent ground, and
- oil, salt, and metals in spent drilling mud.

Occurrence and Movement of the Acid Plume

The Buna Yard driveway has the highest conductivity, highest sulfate concentration, and lowest pH of any area at the Fox Vacuum site and undoubtedly contains the sulfuric-acid source at the Fox Vacuum site. Abovebackground conductivity coincides with the barren ground and, to a lesser extent, the area with stressed vegetation in the pasture. This is direct evidence that the acid-contaminant plume is responsible for the barren ground and stress to remaining grass adjacent to the barren ground. Fortunately, conductivity is at background beyond the zone of stressed vegetation; this shows that contaminant plume is limited in extent to the zone of affected vegetation. The distribution of ground conductivity shown in figure 11 can be used as a proxy for the distribution of sulfuric acid, that is, the concentration of acid is highest where conductivity is highest.

The acid-contaminant plume has percolated to a depth of no more than 10 ft (3 m) throughout the Fox Vacuum site, including beneath the driveway source and the barren ground (fig. 9). This appears to be limited by

the vertical distribution of soil textures (fig. 8). The northwestward movement of the plume away from the driveway is consistent with flow downslope toward the unnamed tributary of Nichols Creek. The ephemeral nature of moisture content in the Kirbyville-Waller soil, which is saturated in winter and spring but dry in summer and autumn, means that lateral transport most likely is episodic. Rapid lateral flow in the uppermost sandy loam (see fig. 8) would occur only in winter and spring, when the ground is saturated. During summer and autumn, the lateral gradient in hydraulic head would decrease, and flow would be downward toward the water table, upward owing to surface evaporation and plant transpiration, or lateral by diffusion. Summer evaporation of moisture from the unvegetated soil of the barren zone might be large.

The zone of elevated conductivity in the vicinity of pits 2 and 3 east of the driveway (fig. 11) probably reflects a moderate salt content of water discharged along with hydrocarbon-contaminated drilling mud (tables 6 and 7) rather than eastward movement of the acid-contaminant plume. The chloride concentrations of 598 and 439 mg/kg in pits 2 and 3, respectively, correspond to electrical conductivities of a few hundred mS/m, which are sufficiently high to produce elevated ground conductivities near these pits. There is no evidence in ground-conductivity data or chemical analyses of well water to support an interpretation that contamination from the Fox Vacuum site has affected the well (no. 1, fig. 4) located 350 ft (106.8 m) east of the site.

# Estimation of Acid Volume

An estimate of the volume of acid contamination is needed to constrain the selection and design of a cost-effective approach to site cleanup.

The mass of contaminant (sulfuric acid) in the subsurface at the Fox Vacuum site can be determined from the electromagnetic geophysical data and the analytical data from the three bore holes drilled at the site. The electromagnetic geophysical data were used to estimate the volume of ground at different electrical conductivities and the analytical data were used to translate apparent electrical conductivity to pH and sulfate concentrations, as follows.

Background electrical conductivity was defined as 43 mS/m on the basis of figure 11. Areas with conductivity greater than 43 mS/m were calculated by cutting away successive contour intervals from a paper copy of the conductivity map. The paper sections were weighed to determine area using the weight of a known area at the map scale. The acid-contaminated area, including the Buna Yard driveway, pits, and Alvarez Road drainage ditch, was found to measure almost 52,500 ft<sup>2</sup>, or 1.2 acres (4,875 m<sup>2</sup>). Figure 14 shows the percent of contaminated area (conductivity > 43 mS/m) having ground conductivity greater than a given value. For example, only 5,250 ft<sup>2</sup> or 0.12 acre (488 m<sup>2</sup>), less than 10 percent of the contaminated area, has conductivity greater than 130 mS/m.

At the high electrical conductivity within the contaminated zone, both pH and sulfate concentration are strongly correlated with electrical conductivity (fig. 15). The correlation breaks down at the low conductivity within the "background area," where there are several controls on pH and sulfate concentration and a variety of contributors to electrical conductivity. The correlation can be used to estimate sulfate concentration within the contaminated zone on the basis of electrical conductivity. End-member values were used to relate ground conductivity measured by the geophysical



Figure 14. Distribution showing percentage of area having ground conductivity greater than a given value.



Figure 15. Relation between electrical conductivity and (a) pH and (b) sulfate concentration measured in core samples from bore holes BEG-1, BEG-2, and BEG-3.

survey to electrical conductivity measured in core samples in the laboratory (table 9).

Table 9. Comparison of end-member conductivities between background and acid-contaminant plume areas.

	EM-survey (mS/m)	Core sample (mS/m)
Background	43	11.57
Maximum contamination	160	586.18

Table 10 shows pH and sulfate concentration calculated from these relationships and the areal extent contained within each range of conductivities. Using 10 ft (3.0 m) as the maximum thickness of the contaminated zone (fig. 9), table 10 shows that the total volume of acid-contaminated ground at the Fox Vacuum site is nearly 516,500 ft<sup>3</sup> (11.9 acre-ft; 19,130 yd<sup>3</sup>; 14,623 m<sup>3</sup>). Assuming a porosity of 20 percent and a liquid saturation of 70 percent yields an estimate of the volume of contaminated pore space of approximately 72,400 ft<sup>3</sup> (2,050 m<sup>3</sup>). Finally, assuming a uniform distribution of contamination with depth, the total mass of elemental sulfur is approximately 770 lb (350 kg). Actual mass of sulfur most likely is less because contamination decreases beneath a depth of 4 ft (1.2 m).

#### Source of Acid

There are two hypotheses for the origin of 770 lb (350 kg) of elemental sulfur at the Fox Vacuum site:
Table 10. Calculation of mass of sulfur contained within acid-contaminated ground at the Fox Vacuum site, based on 10-m ground-conductivity survey.

Ground conductivity (mS/m)	Predicted SO <sub>4</sub> (mg/L)	Predicted pH	Area (m <sup>2</sup> )	Volume⁺ (m <sup>3</sup> )	Pore volume** (m <sup>3</sup> )	Mass SO <sub>4</sub> (kg)
160	9794	1.4	54	161	23	221
140	4742	1.8	163	488	68	324
120	2053	2.2	352	1057	148	304
100	763	2.8	383	1148	161	123
80	227	3.4	445	1335	187	42
60	48	4.3	824	2473	346	16
50	18	4.8	1200	3599	504	9
43	8	5.2	<u>1454</u>	<u>4362</u>	<u>611</u>	5
Total			4,875	14,623	2,048	1,044

Assumes thickness of 10 ft (3 m) Assumes 20 percent porosity and 70 percent saturation

- (1) Oxidation and solution of solid sulfur contained within the material making up the Buna Yard driveway, which might have derived from a sour-gas processing or sweetening plant.

(2) Illegal discharge of a waste liquid consisting of sulfuric acid. It might not be possible to unequivocally distinguish between the two hypothesized sources.

Solid Sulfur Source

H<sub>2</sub>S is a toxic gas contained within natural hydrocarbon gas produced from subsurface gas reservoirs. H<sub>2</sub>S is extracted from natural hydrocarbon gas at sour-gas processing or sweetening plants, yielding elemental sulfur and scale consisting of precipitated impurities from the natural gas (Goar, 1979; Goar and Arrington, 1979). There have been reports of water contamination from rainwater runoff at waste piles of sulfur and scale at processing plants (J. Tintera, personal communication, 1995).

Operators of the Fox Vacuum site might have used the sulfur-scale waste package in place of caliche, gravel, or other road base material for constructing the driveway at the Buna Yard. The sulfur would have been dissolved and oxidized by rainwater containing dissolved oxygen that falls on and percolates into the driveway material according to a reaction such as

$${}^{0}S + 4 H_{2}O = {}^{6+}SO_{4}{}^{2-} + 8 H^{+} + 6 e^{-}$$
(1)

The oxidation reaction might be mediated by bacteria and not be strictly an inorganic reaction.

The driveway material at the Fox Vacuum site might have consisted of the hypothesized sulfur-scale waste when the site was developed between 1958 and 1976. Alternatively, the sulfur-scale waste might have been recently

applied as a top dressing on earlier base material. It is interesting to note, on the basis of aerial photographs, that the barren zone did not begin to develop until after the middle to late 1980's. This leads to the following question: If the sulfur-scale driveway is old, why did the sulfuric acid plume take so long to develop? A top dressing applied during the 1980's seems a likely explanation consistent with the apparently limited extent of acid contamination at the site. Acid contamination in the Alvaraez Road ditch most likely has been transported as particulate sulfur along with runoff from the driveway following storm precipitation.

The volume of 770 lb (350 kg) of elemental sulfur is quite small—6 ft<sup>3</sup> or <0.22 cubic yard (0.17 m<sup>3</sup>). In other words, a small amount of elemental sulfur mixed in a road base material and deposited in the Buna Yard driveway (in fact, less than 1 percent by volume) accounts for the entire amount of dissolved and elemental sulfur at the Fox Vacuum site. The sulfur-scale waste in the Buna Yard driveway appears to be no more than 10 percent sulfur. The acid-contaminant plume represents the leaching of less than 0.2 percent from such a source. Considerable potential remains for generation of additional acid leachate. Treating the acid source in the driveway, therefore, is an essential part of site cleanup.

Liquid Sulfur Source

If a waste acid liquid was discharge at the site, it most likely was sulfuric acid (H<sub>2</sub>SO<sub>4</sub>). Concentrations of nitrate, chloride, and fluoride are low, which eliminates the likelihood that nitric (HNO<sub>3</sub>), sulfamic (H<sub>3</sub>NO<sub>3</sub>S), hydrochloric (HCl), and hydrofluoric (HF) acids might have been present. The volume and strength of a hypothetical liquid waste discharge are, of course, unknown; only a range of reasonable estimates can be made (table 11). The

volume probably ranged from a few 42-gallon (159-L) barrels to one 100-barrel (~560-ft<sup>3</sup>, ~16-m<sup>3</sup>) tanker truck. Dozens of drums would seem less likely than a tanker truck if a large volume of acid had been discharged because of the labor and noise involved in their dumping, and the apparent absence of drums at the site. We assume that only one tanker truck might have involved in an acid release. The acid strength probably would have been between 1 percent (0.2 N, 0.01 kg/L) and 32 percent (12 N, 0.4 kg/L). It seems unlikely that full strength, uncontaminated, 36 N sulfuric acid would have been to be because it would have had economic value as a reagent.

Table 11. Estimation of volume of sulfuric acid at different concentrations needed to account for recorded concentration of contaminant at the Fox Vacuum site.

Source	Waste			
concentration	source volume			
0.2 N	28,183 gallons			
	671 barrels			
	(106,644 L)			
12 N	23.5 gallons			
	0.6 barrels			
	(88.7 L)			

A 100-barrel (~560-ft<sup>3</sup>, ~16-m<sup>3</sup>) volume spilled and evenly distributed on the 15,300-ft<sup>2</sup> (1,422-m<sup>2</sup>) driveway would be 0.44 inches (1.1 cm) thick. Some of the spill would immediately soak into the road base and some would most likely flow down the site drainage to the outfall point at Alvarez Road. The sulfuric acid would have oxidized organic matter (leaves and other tree litter, grease, oil) on the driveway. There probably would have been a significant vegetation kill at the time of the spill that would also have affected part of the Alvarez Road ditch.

Migration of Contaminants from Mud Pits

Crude-oil-contaminated drilling mud is present in pits 2, 3, 4, 6, 7, possibly in pit 1, and along the channel from pit 4 to pit 7. The possible contaminants in the drilling muds at the Fox Vacuum site, including oil, dissolved salts, and heavy metals, are at concentrations less than limits specified to protect public health and safety and the environment. TPH is less than 1 percent and other constituents including PAH's also have low concentrations (tables 7 and 8). The cutoff value for oil-contaminated soil at which excavation for remediation or disposal is required is 1 percent TPH (Rule 91, Railroad Commission of Texas, 1994). The muds have low chloride content (<3,000 mg/L), as indicated by results of the ground-conductivity survey (figs. 10 and 11) and analyses of extractable anions (table 6). The cutoff value for disposal of low-chloride drilling fluid by land farming without a permit is 3,000 mg/L chloride (Rule 8, Railroad Commission of Texas, 1994). Concentration of barium in the drilling mud (<9 mg/L, table 7) is less than the EPA's TCLP regulatory standard of 100 mg/L.

The scope of this investigation did not include sampling soil water or ground water in the vicinity of the mud pits to determine the presence of hydrocarbon-derived contaminants, salt water, or heavy metals. Based on the low concentration of possible contaminants in the mud pits, however, there is negligible grounds for concern regarding risk to public health and safety from pollution of soil water or ground water in the vicinity of the mud pits.

Any movement of possible contaminants from the pits, including crude-oil products, dissolved salts, or heavy metals, most likely would be in

the same direction (northwest) as the acid-contaminant plume. Soil cores taken at the site pad immediately northwest of pits 3 and 4, however, show no evidence of contamination related to migration of pollutants from the oilcontaminated drilling muds (table 4, fig. 3). The low-permeability clay that underlies the site (fig. 8) should retard vertical movement of potential organic contaminants from the drilling fluid disposal pits.

## ENVIRONMENTAL IMPACT ASSESSMENT

## Summary of Assessment Issues

The principal health and safety issues at the Fox Vacuum site that need to be evaluated relate to (1) potential transport of the sulfuric acid contaminant in saturated soil or shallow ground water and (2) pathways for contaminant to reach the biosphere. The potential transport of contaminants from oil-contaminated drilling mud is not an issue of concern because possible pollutants are at less-than-threshold concentrations.

# **Migration Pathways**

The principal concern for the acid-contaminant plume is its ongoing advance through the pasture and its impact on land use and land value because of the expected additional loss of pasture vegetation, impaired nutrient value of some of the grass crop, and risk to livestock health that might be allowed to forage in the zone of stressed vegetation (this area at present is fenced). The potential for erosion and transport of acidcontaminated sediment into the drainage ditch of Alvarez Road is understood to be a secondary concern because such processes to date have had only small impact on sediment chemistry (samples 21 and 22, table 1). Core data shows the acid contaminant has moved no deeper than 10 ft (3 m) below ground surface; most of the contamination has remained in the uppermost 4 ft (1.2 m). The direction of movement is toward the northwest from the Buna Yard driveway; the plume has moved less than 100 ft (30 m). Seasonally saturated soil water at the Fox Vacuum site has been impacted in terms of pH and dissolved sulfate. A pH of 2.0, however, is not in itself indicative of a hazard; many carbonated soft drinks have such a low pH. However, the minimum value of pH allowable for potable waters is 6.5 (De Zuane, 1990). The recommended sulfate limit in drinking water is 250 mg/L. High levels of sulfate can cause diarrhea and dehydration, although after a period of adjustment tolerance to levels even over 400 mg/L can be attained (De Zuane, 1990). There is no evidence, however, for contamination of shallow ground water by sulfuric acid from the Fox Vacuum site.

If sulfuric acid at the site formed from oxidation of elemental sulfur in the Buna Yard driveway, the impact of the acid contaminant has taken several years to be manifested by the advancing barren zone. Without remedial action, elemental sulfur in the driveway will continue to supply the plume. If sulfuric acid was discharged as a liquid, its immediate impact occurred some time ago. It does not appear to have made an acute impact, and there was no record of injury or gross pollution. There remains a lower level of contamination, which is still being diluted by rainfall. The acidcontaminant plume is being only slowly neutralized as it spreads, however, because the Kirbyville and Waller mineral soils have little acid-neutralizing potential.

Although the site is in a rural setting, there are several households adjacent to or down the road from the Buna Yard. The site is fenced and gated

and hazard signs are posted. A fence has been placed separating the barren ground and stressed vegetation zone from the remainder of the pasture where livestock are grazed. Access nonetheless remains relatively open and unauthorized entry might occur.

#### Toxicity

### Sulfuric Acid Effects on Plants

Understanding how sulfuric acid causes physiological stress and ultimately the death of vegetation and the formation of the barren zone at the Fox Vacuum site is needed as a basis for correctly evaluating risk to public health and safety. It is also needed for evaluating and selecting the most appropriate remediation technique.

The fact that plant growth and health are linked to soil pH has been long understood; in fact, the practice of liming soils to raise pH took place in ancient Grecian and Roman agriculture. Acid in the soil environment can have a direct toxic effect on plant roots by loss of membrane integrity. There also can be indirect effects on the bioavailability of nutrients through changed ionic balance, proton competition with metal cations, impacts on soil microorganisms, and increased leachability of nutrient metals. Solubility of aluminum, for example, increases with decreased pH, and high concentrations of aluminum can impair root activity, perhaps by limiting root uptake of other metal cations required as nutrients, such as calcium and magnesium (Binkley and others, 1989). Solubility of other plant nutrients, such as phosphate and molybdenum decreases with decreased pH, which might result in a nutrient deficiency. At low pH, the high concentration of protons (H+)—recall that pH is the negative logarithm of the chemical

activity of the H<sup>+</sup> ion—displaces other metal cations from adsorption sites in clay minerals, which might become unavailable for plant uptake.

Solubility of key nutrients, especially phosphorus (P), might be decreased in the presence of a high concentration of dissolved sulfate; the nutrient could be precipitated in a sulfate salt.

Vegetation adjacent to the barren zone appears stressed (fig. 2). Grass is thin, patchy, more yellow, and not as tall as in the rest of the unaffected pasture, indicating this grass is experiencing physiological stress, most likely owing to a problem in the bioavailability of nutrients. It is possible that the nutrient content of the grass as a forage for livestock is decreased relative to grass unaffected by the acid soil. The area of stressed vegetation makes up approximately 20 percent of the acid-contaminant plume, or 10,500 ft<sup>2</sup> (0.25 acres, 975 m<sup>2</sup>)

### Crude-Oil-Contaminated Mud

Reserve pit solids generally are not hazardous in terms of acute risk to health, public safety, or the environment (Deuel and Holliday, 1994). Spent drilling muds typically contain an excess of metals and organics that might become contaminants in ground water. However, the possible contaminants in the drilling muds at the Fox Vacuum site, including oil, dissolved salts, and heavy metals, are at concentrations less than regulatory limits specified to protect public health and safety and the environment.

# Future Land Use

The potential for future impact is dependent on the use of the Fox Vacuum site, including the Buna Yard and adjacent pasture land. Future impacts would be different for residential use than for agricultural use or

wildlife habitat. The first requires higher standards than the latter two. Here, future use is defined as that prior to oil-field activities at the site, which is essentially undeveloped or rural land used for pasture.

## Fate if Left Alone

## Acid-Contaminant Plume

The natural environment at the Fox Vacuum site has negligible or limited ability to significantly remediate the acid-contaminant plume. The Kirbyville-Waller soils have only slight potential for acid neutralization, as indicated by the differences in pH and sulfate concentration between the Buna Yard driveway and the edge of the barren ground (compare core data from BEG-1 and BEG-2 in figure 9). However, the amount of residual acid within the source area and contaminant plume most likely exceeds the neutralization capacity of the substrate immediately downgradient of the site. Therefore, the barren ground is expected to advance farther northwest yearly, claiming more and more of the pasture west of the Buna Yard.

The ultimate fate of the acid-contaminated soil water probably will be to discharge into ephemeral surface water standing in low areas at the north end of the pasture adjacent to the Fox Vacuum site, and then to drain into an unnamed tributary of Nichols Creek. In April 1995 the standing water at the north end of the pasture had a pH of 6.0; there is no evidence that the acid plume has yet migrated that far. Runoff from the driveway is be expected to continue to add sulfur having acidizing potential to the Alvarez Road drainage ditch. These impacts will be chronic, rather than acute, however, and will include more and more area if no action is taken.

With continued loss of vegetative cover the potential for and magnitude of soil erosion and gullying increases. Runoff will transport some of the eroded sediment into the Alvarez Road drainage ditch.

Because the acid-contaminant plume has yet moved to depths greater than 10 ft (3 m), perhaps because the surficial loam is underlain by a clay layer (fig. 8), the risk for significant vertical transport in the near future seems small. In general, the Montgomery Formation at the site is clay rich and as much as 100-ft (30-m) thick, limiting vertical recharge to the main part of the Chicot aquifer (fig. 5). There are no shallow ground-water wells northwest or downgradient of the advancing contaminant plume.

## Crude-Oil-Contaminated Mud

Drilling muds in earthen pits at the Fox Vacuum site contain petroleum hydrocarbons, salt water, or heavy metals at concentrations of less than the limits specified to protect public health and safety and the environment. There is no regulatory requirement for removal or cleanup of the spent drilling fluids at these low levels of contamination. We conclude, therefore, that risk to public health or safety from migration of possible contaminants from the earthen pits is expected to be negligible under the noaction alternative, that is, if the spent drilling muds are left alone and not excavated or treated.

Transport of organic or other contaminants at low concentrations in a possible subsurface plume emanating from the earthen pits can compared to the flow of the acid-contaminant plume. Flow most likely would be to the northwest. There is, however, no evidence of contamination related to migration of pollutants from the oil-contaminated drilling muds in the analyses of soil cores taken beneath the site pad immediately northwest of pits

3 and 4 (table 4, fig. 3). The low-permeability clay that underlies the site (fig. 8) should retard vertical movement of potential organic contaminants from the drilling fluid disposal pits. There might have been little flux of fluids out of the drilling muds because of their high water-holding capacity. Natural processes probably have retarded the advance of any organic-contaminant plume. It is probable that some natural biodegradation has occurred within the pits. In situ natural processes, including bacterial degradation, oxidation, dehydration, compaction, and flushing of salts, have only affected the uppermost part of the spent drilling fluids, forming a solid 1-ft-thick (0.3-m) crust in all pits. The water-logged and most likely anaerobic environment, however, has limited the in-place degradation of the crude oil.

#### **REMEDIATION ALTERNATIVES**

### Cleanup Criteria

The sole contaminant of concern at the Fox Vacuum site requiring remediation is the sulfuric acid in the Buna Yard driveway and adjacent ground. Crude-oil-contaminated drilling muds at the Buna Yard do not require action because levels of possible contamination (in terms of total petroleum hydrocarbons, chloride content, and heavy metals) are below regulatory limits. The objective of risk-based remediation is to eliminate or reduce to the maximum extent practicable any substantial present or future threat to public health and safety. For the Fox Vacuum site this means managing the source of sulfuric acid and the subsurface sulfuric-acid plume.

For treating or neutralizing the acid, the logical cleanup criterion is a buffered soil pH in the same range as background (4.5 to 6 [Neitsch, 1982]) to allow vegetation to regrow. It is assumed that some level of remaining

contamination is acceptable if risk to public health and safety and the environment can be shown to be sufficiently small. Accordingly, if the acid contamination is managed such that vegetation can be restored, there might be no further requirement to control the concentration of dissolved sulfate in the ground. Some added cleanup of dissolved sulfate in the form of precipitated gypsum might occur during the course of acid neutralization.

#### **Target Areas**

There are no acute or emergency impacts of contaminants at the Fox Vacuum site and chronic contamination began some time in the past. The two target areas at the Fox Vacuum site include (1) the site pad or driveway of the Buna Yard, which encompasses the source of the sulfuric acid, and (2) the acid-contaminant plume underlying the area with barren soil and stressed vegetation on the adjacent property. Different waste-management options are possible for the two target areas and are considered separately where appropriate to maximize the cost-effectiveness of cleanup measures. Cleanup will be organized in stages. The first stage is to address the source of contamination; neutralizing 29 percent of the affected ground—the 15,300 ft<sup>2</sup> (1,422 m<sup>2</sup>) driveway—eliminates 97 percent of the contamination (table 10). The second stage is to control the acid-contamination plume beneath the barren soil and stressed vegetation area. This would be futile, however, without first neutralizing the source of acid in the Buna Yard driveway. A final optional stage of remediation is to reestablish the fertility of the barren ground in the pasture to allow grass to grow and to control erosion and transport of any remaining contaminated sediment. Control of runoff from the driveway might also be required to minimize future impacts on water quality in the Alvarez Road drainage ditch.

## Technologies

No new technology is needed to manage the sulfuric acid at the Fox Vacuum site. The acid contamination is similar to contamination from mine soils and from acid sulfate soils in drained swamp land. Treatment accordingly can be based on successful practices developed over decades for those more well-known problems. Waste-management approaches include (1) taking no action, (2) excavating the contaminated soil for disposal, (3) neutralizing the contaminant, and (4) putting a barrier around the contaminated ground. The acid in the ground might be neutralized by inplace application of limestone, in-place soil flushing, or soil washing, although the first approach clearly is the most cost-effective for the Fox Vacuum site. A barrier could be a physical barrier preventing further migration of the acid plume or a reactive barrier that consumes the acid as contaminated soil water passes through. Cost estimates in the following are based on unit and assemblies costs cited in ECHOS (1995).

## No Action Alternative

The "no-action" alternative for dealing with the sulfuric-acid contamination most likely leaves unacceptable risk to public health and safety and the environment and therefore is considered unacceptable. Natural soil processes are inadequate to neutralize the acid and reduce risk within a reasonable time. The environmental impact assessment concluded that the no-action alternative would result in continued advance of the barren ground to the northwest across the pasture with probable discharge to ephemeral surface water. The main impact of the acid-contaminant plume will be an increase in the amount of barren ground subject to erosion and a decrease in land value because forage pasture is removed from use. It is

unlikely that ground-water wells, however, either at shallow depth in the Montgomery Formation or at greater depth in the main part of the Chicot aquifer, are at risk for contamination.

Because contaminants in the spent drilling mud are below action levels, the "no-action" alternative for managing that waste material is acceptable for the earthen pits at the Fox Vacuum site.

### Excavation for Disposal

One management option for the acid-contaminated soils at the Fox Vacuum site is to use commercial transportation and landfill-disposal services. This is one of the most expensive alternatives. Cost estimates for excavating, loading, and transporting the contaminated soil for offsite disposal range from \$43 per yd<sup>3</sup> for nonhazardous material to \$75 to \$90 per yd<sup>3</sup> for hazardous material (ECHOS, 1995). The volume of acid-contaminated ground within zone 1, extending to a depth of approximately 4 ft (1.2 m) and containing the main body of contamination, is approximately 61,200 ft<sup>3</sup> (2,300 yd<sup>3</sup>; 1,700 m<sup>3</sup>) beneath the Buna Yard driveway. Total cost for the Buna Yard materials range from \$99,100 to \$207,000. Using this approach for the 148,700 ft<sup>3</sup> (5,500 yd<sup>3</sup>; 4,100 m<sup>3</sup>) acid-contaminant plume on the adjacent property would add another \$236,500 to \$495,000, increasing the total to \$335,600 to \$702,000. The gradational contamination between a depth of 4 and 10 ft (1.2 and 3 m) is not addressed by this approach.

# Acid-Neutralization

In-Place Application of Limestone

The key advantages of this alternative are that it has low cost and generates no additional waste product. In-place application of limestone takes

a somewhat passive approach to neutralizing the sulfuric acid. The technique is to work a predetermined amount of powdered limestone into the soil and then simply leave the site alone. The neutralizing reaction will gradually be completed as acidic soil water comes into contact with the limestone. Acid neutralization at the Fox Vacuum site can be considered an extreme case of soil-pH adjustment.

The amount of needed limestone can be estimated from the data presented in table 10. The mass of sulfate contained within the Buna Yard driveway is calculated to be approximately 1,016 kg (table 10), which corresponds to 10,583 moles of sulfate (SO<sub>4</sub> has a gram formula weight of 96 g/mole and 1 mole contains 6.023 x  $10^{23}$  molecules). Because sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) has 2 protons for each sulfate molecule, there would be 2 x 10,583 = 21,166 H<sup>+</sup> moles. To neutralize one mole of acid requires one mole of limestone (CaCO<sub>3</sub>) or one-half mole of dolomitic limestone (CaMg(CO<sub>3</sub>)<sub>2</sub>):

$$CaCO_3 + H^+ = Ca^{2+} + HCO_3^-$$
 (2)

$$CaMg(CO_3)_2 + 2 H^+ = Ca^{2+} + 2 HCO_3^-$$
 (3)

The weight of 21,166 moles of limestone (calcite) is 4,666 lb (2.1 metric tons).

The effectiveness of applied limestone depends on how finely ground it is and how well and deep it is mixed into the soil. A finely ground limestone is used, with the specification that 90 percent will pass through a 10-mesh screen and 50 percent through a 60-mesh screen (Lyle, 1987). Mixing the applied limestone to a depth of 2 ft (0.6 m) would immediately target the upper half of zone 1 with the highest contamination (fig. 9). Excess limestone would gradually neutralize the acid occurring at depths of 2 to 4 ft (0.6 to 1.2 m) in zone 1 and in the underlying zone 2 (fig. 9). Scarifying and working the limestone into the soil to a greater depth would bring more rapid results.

Although this would be an exothermic reaction, because the reagent is applied dry the reaction proceeds slowly with each rainfall event. The site would be left uncovered to allow rainwater to transport the dissolved alkaline solution to the acid-bearing parts of the soil. While application of limestone neutralizes acidity, excess calcium (equation 2 or 3) is available to precipitate excess sulfate as gypsum.

In comparison, as little as 138 lb (0.06 metric tons) of limestone would be required to neutralize the sulfuric acid in the acid-contaminant plume away from the Buna Yard driveway. This estimate is based on all "abovebackground" conductivity measurements, including those around pits 2 and 3, which reflect salt content rather than sulfuric acid. This is less than the standard prescription of 800 lb (0.4 metric tons) of limestone per acre for soil pH adjustment. The difference is acid neutralization in a poorly buffered mineral soil versus modifying the pH buffer of the soil itself. In comparison, the Buna Yard driveway requires 17 times as much limestone, or 4,666 lb (2.3 metric tons) per 0.35 acres. For small sites such as this, application of limestone is most efficient by the bag rather than by bulk. The site would require about sixty-four (64) 75-lb bags of limestone.

Excess limestone will be applied in order to neutralize existing acid solution as well as to leave the potential to neutralize acid generated in the future by the remaining elemental sulfur. While the gradational contamination between a depth of 4 and 10 ft (1.2 and 3 m) is not immediately attacked by this approach, water percolating through the lime-enriched soil will be alkaline, that is, it will have some acid-neutralizing capacity, and is expected to move through the zone-2 gradational edge of the acid plume.

The application of finely ground limestone has several benefits besides raising pH. It supplies calcium, increases availability of phosphorus, and promotes dispersion of clays and improves physical properties of soil (Lyle, 1987). Dolomitic limestone (CaMg(CO<sub>3</sub>)<sub>2</sub>) might be used instead of calcitic limestone (CaCO<sub>3</sub>) to supplement available magnesium.

Work areas involved in this cleanup method includes purchasing and laying out bags of powdered limestone across the Buna Yard driveway and barren ground in the adjacent pasture (\$700 to \$1,000), scarifying and discing to work the limestone into the soil (\$1,500 to \$2,000), and regrading and leveling (\$200 to \$500). Total cost should be on the order of \$2,400 to \$3,500.

### In-Place Soil Flushing

Soil flushing removes soil contaminants by circulating a basic-pH aqueous solution through the soil and recovering the flushing solution from the target zone for recycling or treatment. This approach requires extraction wells or french drains, an irrigation or injection system, water treatment, and sampling and analysis to manage the treatment and recovery process. Disadvantages of this approach are its cost and its generation of a liquid waste product. Soil flushing is a labor- and capital-intensive approach to neutralizing the acid in place. Costs for constructing the irrigation and recovery plumbing, pumping, and treatment system will be approximately \$20,000. Operation will most likely cost in excess of \$2,000 per month. The period of operation needed for neutralizing acid and attaining the cleanup criterion depend on the sweep efficiency. It is generally expected that 5 to 50 pore volumes need to be flushed through the system to effect complete recovery. At a flow rate of 100 gallons per minute (gpm), it would take almost 4 days to circulate 1 pore volume through all the contaminated ground to a

depth of 10 ft (3 m). Thus, the soil flushing operation might have to run for 1 to 7 months at 100 gpm. It is obvious that construction and operation costs exceed those for application of dry limestone and passive neutralization.

## Ex-Situ Soil Washing

Soil washing is a water-based process for mechanically scrubbing and leaching waste from contaminated soil for recovery and treatment (ECHOS, 1995). The approach requires excavating the contaminated soil, treating it in containers, disposing of the wash solution, and replacement of the cleaned soil on the ground. The ECHOS (1995) cost estimate is approximately \$112 per ton. The zone-1 contaminated soil (fig. 9) beneath the Buna Yard driveway probably weighs about 2,800 ton, giving an estimated cost of \$313,600. The zone-1 contaminated soil beneath the barren ground in the adjacent pasture weighs about 6,900 ton, giving an estimated cost of \$772,800, which adds up to \$1,086,400 for site treatment. The gradational contamination between a depth of 4 and 10 ft (1.2 and 3 m) beneath the zone-1 contamination interval would not be addressed by this limited excavation.

### **Plume Barrier**

A barrier could be a physical barrier preventing further migration of the acid plume or a reactive barrier that consumes the acid as the contaminated soil water passes through.

# **Physical Containment**

Physical containment probably would be ineffective at the Fox Vacuum site. At some settings in water-table aquifers it is cost-effective to leave the contaminant in place but contained from further movement. This usually is achieved by capping or covering the contaminated ground or waste package

with a low-permeability barrier or installing lateral barriers to flow or both. A clay or asphalt cover could be placed over the Buna Yard driveway. This would prevent infiltration of rainwater and reduce the flux of acid out of the road base, but would have little or no effect on the acidity of the covered material or its further movement. The acid-contaminant plume is moving in the down-gradient direction. Although the steepness of that gradient and velocity of flow might be reduced by placing a cap over the site, soil-water flow would most likely continue unabated. Containment, therefore, would require placing a low-permeability barrier in advance of the acid plume.

Engineered barrier walls, such as iron-sheet pilings or low-permeability clay-slurry walls, have been shown to be effective in water-table aquifers where the barrier can be seated on the low-permeability base of the aquifer. They are most suitable where the plume is large or complex in heterogeneous soils. At the Fox Vacuum site, however, the acid contamination is in an ephemerally saturated soil zone. A lateral barrier probably would have the effect of "backing up" the flow of soil water and cause a greater vertical flux downward to the water table in the Montgomery Formation. Thus, the containment alternative is not a feasible option for dealing with the acidcontaminant plume at the Fox Vacuum site.

### **Reactive Barrier**

A reactive barrier can be envisioned as a back-filled trench around the downgradient margin of the contaminated ground. The backfill material will be a granular porous material such as crushed limestone that allows soil water to pass through but which has excess acid-neutralization capacity. If the trench targeted only the zone 1 contamination it would most likely protect the remainder of the pasture. This approach, however, does nothing to

cleanup the existing contamination beneath the barren ground and, accordingly, is considered an unacceptable alternative.

### Monitoring and Testing

Further monitoring and testing of soil quality will be conducted to document effectiveness of cleanup and site quality prior to closure. This task is separate from operations monitoring, for example, during soil flushing or soil washing. Costs involve mobilizing a 2-person technical crew to use hand augers to collect soil samples and to analyze soil water pH by the extract method. Tests done quarterly for the year following treatment should be adequate to document that cleanup was successful.

## RECOMMENDATIONS

At the Fox Vacuum site, the shallow acid-contaminated soil beneath the Buna Yard (the source) and the adjacent barren pasture ground (the contaminant plume) require remediation. Crude-oil-contaminated drilling mud does not require treatment because possible contaminants of concern are below regulatory limits. Table 12 summarizes the remediation alternatives.

The recommended alternative for treating acid contamination at the Fox Vacuum site is in-place limestone application. The advantages of this approach are its low cost (less than \$5,000) and the fact that it does not generate any additional solid or liquid waste. For the small acreage of the site, the limestone can be applied in 75-lb bags. The estimated number of bags needed is about 64. Applying excess powdered limestone is not a problem, and is even desirable as added surety that acid generated by the remaining elemental sulfur at the site will also be neutralized. Once the limestone is worked into the soil, the neutralization is a passive process that takes place

## Table 12. Comparison of remediation alternatives for the Fox Vacuum site.

Remediation alternative

No action

Advantages/ Disadvantages

Not acceptable for acid contaminated soil because of impact. Acceptable for spent drilling mud in earthen pits

Costly. Targets zone-1 contamination only

Capital and labor intensive.

Capital and labor intensive.

Cleanup of zone 1 only.

No cleanup performed.

reclaim pasture for use.

impact

zone 2 contamination.

In-place limestone neutralization

Excavate and dispose

Low cost. No additional waste product generated. Targets zone-1 contamination but eventually acts on zone-2 contamination.

Generates additional waste for disposal. Targets zone 1 but likely also reaches

Generates additional waste for disposal.

Not likely to be completely effective

Needed to control soil erosion and

No cleanup of existing contamination.

Protects remainder of site from further

In-place soil flushing

Ex-situ soil washing

Physical barrier

Reactive barrier

Revegetation

More than \$34,000

Estimated

cost

\$99,100 to \$207,000 for

\$236,500 to \$415,000 for soil in off-site acid plume

driveway material;

Less than \$5,000

\$313,000 for Buna Yard driveway source material; \$772,800 for soil in off-site acid plume

Not estimated

Not estimated

\$500

gradually and continuously as moisture becomes available to move the acid solution through the soil to encounter the powdered limestone.

Other alternatives, including excavation for landfill disposal, in-place soil flushing, and ex-situ soil washing, are at least 5 to more than 20 times as costly and do not readily attain as high a level of cleanup.

The flux of sulfuric acid undoubtedly damaged or destroyed the fertility of soil in the barren part of the pasture adjacent to the Buna Yard. Once the acid is neutralized, soil fertility must be restored before land reclamation will be complete. This will require application of fertilizer and replacement of organic matter (the latter having been oxidized by the acid). The estimated cost for hydromulch seeding and fertilizing for the 0.85 acre area is \$430 (ECHOS, 1995).

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#### APPENDIX

# **BID INFORMATION**

The RRC is soliciting TURNKEY BIDS for the purpose of conducting site cleanup and restoration activities at the referenced site. This turnkey bid shall include all personnel, equipment, goods, and services necessary to access the location and remediate the site per procedures defined under services to be performed. The turnkey bid shall include any site preparation, access to and egress from the site including any road building or special access problems. Bids will be awarded to the lowest turnkey bidder capable of performing services as specified.

LOCATION: From Buna, Jasper County, Texas, Fox Vacuum site, also referred to as the Buna Yard in RRC files (Site No. 93-03-0019), is in Jasper County, Texas, RRC District 3, approximately 9.2 miles (15 km) south of Kirbyville and travel north on US Highway 96 8.0 miles (13 km), turn right on Alvarez Road and go east 0.4 miles (0.64 km). Lease gate is barred and chained.

**NOTICE TO BIDDERS:** Contractors are encouraged to inspect the site before submitting bids. This site will be available for viewing on \_\_\_\_\_\_

Those interested in inspecting the site must contact the Austin Railroad Commission Office at 512/463-6765 prior to viewing date and prior to entering the site. Bids must be received at the Austin Office by 3:00 p.m. on \_\_\_\_\_

\_\_\_\_\_

Bidders may attend bid opening at

in the Austin Railroad Commission Office, 1701 North Congress, William Travis Building, 11th Floor.

KNOWN SITE DATA: Site is abandoned drilling pit facility with a site pad road base that is contaminated by elemental sulfur from a sour-gas processing plant. Rainfall has dissolved sulfur and formed in the soil zone a dilute sulfuric acid with pH as low as 1.0. The site is underlain by a sandy loam soil to a depth of about 10 feet with a clay pan at a depth of about 3 feet. Movement of the acid in the soil zone has killed about 1/2-acre of grass in the pasture adjacent to the facility. The facility site pad measures approximately 15,300 square feet (0.35 acre) and the adjacent barren pasture measures approximately 21,780 square feet (0.5 acre). A 2-foot high berm with pine trees and an old barbed-wire fence separates the two areas. A few pieces of steel pipe lie on the ground at one corner of the site and one or more pieces of pipe may be buried beneath the site.

### **KNOWN REQUIREMENTS:**

{This section contains standard RRC requirements.}

SERVICES TO BE PERFORMED: The objective of the work is to neutralize the sulfuric acid in the soil by applying and working powdered limestone (CaCO<sub>3</sub>) into the ground to a depth of at least two (2) feet across the facility site pad and that part of the adjacent property designated as the barren ground as caused by the acid contamination of soil. The required scope of services includes the following.

 Purchase and transport to the site 6,000 pounds (for example, eighty 75pound bags) of finely ground limestone (CaCO3) meeting the following size specification: 90 percent (by weight) will pass through a 10-mesh screen and 50 percent through a 60-mesh screen.

- 2. Scarify the soil surface to a depth of 2 feet, for example using a graderscarifier and disc harrow.
- 3. Spot bags at 15-foot center spacings across the site pad (total of 75 bags) and at 50-ft center spacings across the barren ground (total of 5 bags).
- 4. Open the limestone bags and empty into piles. Level the piles evenly, for example, by hand raking or with a drag pulled by a tractor.
- 5. Immediately after spreading the limestone spray with water to reduce dusting, using water brought to the site by truck.
- 6. Mix the limestone into the scarified ground
- 6. Collect and secure all empty bags and remove them for disposal by permitted means.
- 7. Uniformly mix the spread-out limestone powder into the top 2 feet of the soil using a rotary mixer. Uniform mixing will be determined by visual observation.
- 8. Grade and level the facility site pad driveway and the adjacent pasture ground.
- 9. Using 15 cubic yards of clean dirt brought to the site, erect an earthen berm approximately 50-feet long, 2-feet high, and 4-feet wide across the entrance to the site and tie the berm tied the existing berms to contain runoff.
- 10. Prior to scarifying soil at the site, contractor will be responsible for locating all lines (pipelines, utility lines, etc.) and discarded sections of pipe above or below the ground surface at the site. Site activities will be coordinated to avoid puncturing or severing lines. The contractor will

submit in writing that all lines have been located and marked prior to excavation.

11. All work will be conducted during daylight hours on a daily basis excluding weekends until job is completed. Contractor will provide 48hour notice to RRC prior to beginning site work. Work will be conducted continuously, weather permitting, with work completed within a maximum of one week.