LEAKING UNDERGROUND STORAGE TANKS:

SITE CHARACTERIZATION,

REMEDIATION AND

RISK ASSESSMENT

Ву

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# SITE CHARACTERIZATION,

# REMEDIATION AND

# RISK ASSESSMENT

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iii

# TABLE OF CONTENTS

Chapte	r Pa	age
I.	INTRODUCTION	1
II.	LITERATURE REVIEW	5
	Background History	5
	Site Characterization	6
		8
	Remediation	10
III.	SITE CHARACTERIZATION	12
	Introduction	12
	Contaminant Migration Pathways	13
	Soil	19
	Groundwater	$24^{-2}$
		~ .
IV.	REMEDIATION	34
	Introduction	34
	Physical Control Measures	37
	Source Control	37
	Solidification	38
	Well Systems	39
	Interceptor Systems	41
	Subsurface Barriers	42
	Surface Capping and Liners	44
	Treatment of Contaminated Soil	44 45
	Excavation and Disposal	45 45
		43 47
	Landfarming/Enhanced Volatilization	
	Incineration	49
	Soil Vapor Extraction	50
	Soil Washing/Extraction	51
	Microbial Degradation	53
	Treatment of Contaminated Groundwater	56
	Air Stripping	56
	Carbon Adsorption	58
	Biological Treatment	59
	Treatment Trains	62

Chapter

v.	RISK ASSESSMENT 63
	Introduction $\ldots$
	Source/Release Assessment
	Exposure Assessment
	Dose-Response Assessment 70
	Risk Characterization 71
VI.	CASE STUDY
	Introduction
	Background Information 72
	Site Characterization
	Location and General Physiology 73
	Site Description
	Soil
	Groundwater
	Remediation
	Bioremediation Study 92
	Corrective Action Plan 99
	Slurry Wall
	Soil Excavation
	Characterization of Site
	Hydrogeology
	Groundwater Remediation System 114
	Risk Assessment
	Removal Process
	Selection of Chemicals for
	Evaluation
	Exposure Assessment
	Exposure Pathway Analysis
	Identification of Exposure
	Sources
	Identification of Exposure
	Routes
	Pathway Analysis Summary 122
	Estimation of Exposure Concentration 123
	Inhalation
	Dermal
	Estimation of Human Intake 125
	Inhalation
	Dermal
	Risk Characterization
	Noncarcinogenic Health Risk 127
	Carcinogenic Health Risk 128
	Discussion of Health Risks 128

Chapter

Page
------

VII.	DISCUSS	SION	• •	•	• •	•	•	•	•	•	•	•	•	•	•	•	•	•	•	130
	Init	tial	Res	spon	se		•													130
	Init	tial	Aba	tem	ent	Me	eas	ur	es	a	nd	l S	Sit	e	Cł	nec	zk	•	•	131
		tial																		
	Site	e Cha	arac	ter	iza	tic	n	•	•	•	•	•	•	•	•	•	•	•	•	134
																				136
		Sit	ce №	laps	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	136
		So	11.	•	• •	•	•	•	•	•	•	•	•	•	•	•	•	•	•	137
																				139
																				143
																				144
		Ana	alyt	cica	l D	ata	ιS	he	et	S	•	•	•	•	•	•	•	•	•	144
																				144
																				145
		Rer	nedi	.ati	on .	Alt	er	na	ti	ve	s	•	•	•	•	•	•	•	•	145
		e Pro																		
	Cori	rect	lve	Act	ion	P]	.an	L	•	•	•	•	•	•	•	•	•	•	•	146
		lic I																		
VIII.	SUMMARY	AND	CON	ICLU	SIO	NS	•	•	•	•	•	•	•	•	•	•	•	•	•	149
BIBLIO	GRAPHY	• •	• •	•	• •	•	•	•	•	•	•	•	•	•	•	•	•	•	•	153
APPEND	ICES .	• •	• •	•	• •	•	•	•	•	•	•	•	•	•	•	•	•	•	•	159
	APPEN	VDIX	Α-											-						
				PR	OCE	DUF	RES	F	'OR	D	ET	'EC	TI	ON	I					
				MO	NIT	ORI	NG	ł	•	•	•	•	•	•	•	•	•	•	•	160
	APPEN	VDIX	в -	• ОТ	HER	IN	IDU	SI	'RI	AL	W	AS	STE	;						
				$\mathbf{LA}$	NDF	ILI	S	•	•	•	•	•	•	•	•	•	•	•	•	164

# LIST OF TABLES

Table	Page
I.	Record Keeping of Water Level Measurements for Pumping Well
II.	Record Keeping of Water Level Measurements for Observation Wells
III.	Potential Exposure Sources
IV.	Matrix of Potential Exposure Pathways 123
۷.	BTX Vapor Concentrations in the Excavation of USTs
VI.	BTX Percentages in Gasoline
VII.	Daily Intake vs. Acceptable Daily Intake 127

# LIST OF FIGURES

Figu	re				Page
1.	Contaminant Phases in the Saturated Zone	•	•	•	14
2.	Seepage of Oil Through the Soil Zone	•	•	•	15
3.	The Effect of Density on Contaminant Plume Migration	•	•	•	18
4.	Log of Soil Boring	•	•	•	20
5.	Chain of Custody Record	•	•	•	23
6.	Standard Groundwater Monitoring Well	•	•	•	26
7.	Potential Initial Response Situations and Corrective Actions	•	•	•	36
8.	Sources of Groundwater Contamination	•	•	•	67
9.	Project Site Vicinity Map	•	•	•	74
10.	The Fall Line	•	•	•	75
11.	Project Site Map	•	•	•	77
12.	Log of Soil Boring	•	•	•	79
13.	Chain of Custody Record	•	•	•	81
14.	TPH Analytical Results	•	•	•	82
15.	BTEX Analytical Results	•	•	•	83
16.	Soil Boring and Monitoring Well Location Map	•	•	•	84
17.	Soil Isopleth Map	•	•	•	86
18.	Groundwater Monitoring Well	•	•	•	87
19.	Groundwater Contour Map	•	•	•	90
20.	Groundwater Contamination Contour Map	•	•	•	91

21.	Oxygen Uptake Results for Groundwater	95
22.	Oxygen Uptake Results for Pit Soil	96
23.	Oxygen Uptake Results for Peripheral Soil	97
24.	Remediation Site Map	102
25.	Time - Drawdown Graph	107
26.	Distance - Drawdown Graph	110
27.	Radius of Influence	112
28.	Cone of Depression	113
29.	Groundwater Remediation System	115

#### CHAPTER I

## INTRODUCTION

Groundwater is a valuable drinking water resource in the United States in both availability and quality. It is available in quantities large enough to supply 50 percent of the nations population. Due to the nations large dependence on groundwater as a natural resource it is critical to protect this resource.

Existing Federal authority to address groundwater quality problems is present in at least eight statues;

National Environmental Policy Act of 1970 (NEPA) Federal Water Pollution Control Act of 1972 (FWPCA) Toxic Substances Control Act of 1972 (TSCA) Resource, Conservation and Recover Act of 1976 (RCRA) Clean Water Act of 1977 (CWA) Surface mining control and Reclamation Act of 1977 Safe Drinking Water Act of 1979 (SDWA) Comprehensive Environmental Response, Compensation and Liability Act of 1980 (CERCLA). (EPA/625/4-85/016)

One of the largest sources of groundwater contamination comes from underground storage tank systems across the nation. Several million underground storage tank systems (UST's) in the United States contain petroleum. Hundreds of thousands of these UST's, including their piping, are currently leaking (USEPA, June 1987). Many more are expected to leak in the future. Not only can leaking UST's cause fires or explosions that threaten human safety, in addition, leaking UST's can contaminate nearby groundwater.

Congress responded in 1984 to the danger of leaking UST's by adding Subtitle I to the Resource Conservation and Recovery Act. Subtitle I requires EPA to develop regulations to protect human health and the environment from leaking UST's and specifically mandates requirements for financial responsibility (EPA/530/UST-88/005). The EPA is responsible for developing "requirements for taking corrective action response to a release from an underground storage tank" {Section 9003(c) (4)} and "requirements for reporting of releases and corrective action taken in response to a release from an underground storage tank" {Section 9003 (c) (3)}. Section 9001 (5) defines release as " any spilling, leaking, emitting, discharging, escaping, leaching, or disposing from an underground storage tank into groundwater, surface water, or subsurface soils (PEI Assoc. Inc., 1988).

Part 280 of Title 40 of the Code of Federal Regulations gives EPA Technical Standards and Corrective Action Requirements for Owners and Operators of Underground Storage Tanks. The regulations were effective December 22, 1988, and the Office of Underground Storage Tanks in the EPA is to implement these broadly defined rules. The office has implemented a ten (10) year phase in period of underground storage tanks. By December 22, 1998 all Underground Storage Tanks storing petroleum hydrocarbons should be in compliance. At that time all UST's and associated piping will comply with (1) cathode protection , (2) leak detection, (3) spill and overfill protection and (4) financial responsibility (\$1 - 2 million per occurrence). "Per Occurrence" means the amount of money that must be available to pay the costs of one occurrence (EPA/530/UST-88/005).

At many UST sites, remediation of the soil and groundwater have not been effective and do not met the cleanup goals. The main reason is due to initial site characterizations that have either not been done properly or in not enough detail. This has given rise to the question of which remedial alternative is best. In addition to cleanup of the environment, the EPA is concerned with the contaminants risk to human health. The science of risk assessment has been introduced and needs to be characterized for leaking USTs. This investigation gives technical factors that need to be addressed in a proper site characterization. Remedial technologies are presented for different situations and a risk assessment has been conducted targeted on the engineers and contractors working with leaking USTs.

## CHAPTER II

#### LITERATURE REVIEW

The literature reviewed for this thesis included articles from journals, books, federal and state documents, class notes and material handed out in graduate courses, and personal communications with federal and state agencies. The search was conducted on three broad subjects; site characterization, remediation, and risk assessment concerning leaking underground storage tanks. Information and data were obtained from a site in Washington, D.C., and a case study conducted.

#### Background History

In 1984, Congress responded to the danger of leaking USTs by adding Subtitle I to the Resource and Conservation and Recovery Act (RCRA) of 1980 (EPA/530/UST-88/008). In September of 1985, USEPA published a Seminar Publication for protecting public water supplies from groundwater contamination, including USTs (EPA/625/4-85/016). Gasoline spills from leaking USTs are a serious concern due to their widespread occurrence and the acute toxicity of gasoline

hydrocarbons (ex: benzene, known carcinogen)(PEI Associates, Inc., 1988). Hundreds of thousands of USTs, including their piping are currently leaking (USEPA, June 1987). In September 1988 the USEPA published the technical requirements for USTs to be in compliance under regulations effective December 22, 1988 (EPA/530/UST-88/008). In December 1988, the USEPA published the financial responsibilities to owners/operators of USTs (EPA/530/UST-88/005).

#### Site Characterization

Before UST regulations, site characterization of a contaminated site was found in the <u>Seminar Publication of</u> <u>Protection of Public Water Supplies from Ground-Water</u> <u>Contamination</u>, EPA/625/4-85/016, published in September of 1985. In June 1986, the effects of residual gasoline in unsaturated aquifer materials was studied (Hoag et al, 1986). The National Water Well Association, September of 1986, published a technical enforcement guidance document to help regulatory agencies and management in the field of groundwater pollution at Superfund sites (NWWA, 1986). In March 1987, the EPA through the Robert S. Kerr Environmental Research Laboratory released its findings on groundwater from a hydrogeologic perspective (EPA/625/6-87/016). By this time, research had been conducted on the processes affecting subsurface transport of leaking

underground tank fluids, by the Environmental Monitoring Systems Laboratory in June 1987 (USEPA, June 1987).

Arthur L. Baehr released information on the selective transport of hydrocarbons in the unsaturated zone (Baehr, October 1987). Driscoll through the help of the Johnson Division, published an excellent book, <u>Groundwater and</u> <u>Wells</u>. This book addressed hydrologic characterization procedures, through the experience and knowledge of the water well industry (Driscoll, 1987).

In 1988, C.W. Fetter's book, Applied Hydrogeology, added to the available knowledge of site characterization of groundwater (Fetter, 1988). Many publications became available in 1990 towards the understanding of hydrocarbons in the subsurface. These included the fate and transport of petroleum under biotic and abiotic conditions (Carberry and Lee, 1990); the importance of pumping tests in site characterizations (Butler, May-June 1990); assessing UST corrective action technologies for the saturated zone (Reidy, June 1990); the volatilization of organic compounds in unsaturated media during infiltration (Cho et al, 1990); the retention of diesel fuel under different parameters in aquifer media (Kia and Abdul, July 1990); and the groundwater contamination caused by the vapor transport of volatile organics (Mendoza and McAlary, 1990). H.B. Kerfoot, in 1991, studied the partitioning of volatile organics in the subsurface and their effects to temperature and porewater content (Kerfoot, 1991). A new soil sampling technique of residual gasoline by intact stainless steel core sleeves versus field barrel extrusion was conducted (Ostendorf et al, Spring 1991).

## Remediation

Remediation technologies for gasoline contaminated soil and groundwater has been addressed as a part of many industrial treatment processes of waste before specific applications to USTs.

EPA began studying the effects of biotechnology with a series of workshops in 1978, 1979 and 1980 (EPA/600/J-87/007). Kavanaugh and Trussell emphasized the proper design of aeration towers to strip volatile contaminants from drinking water (Kavanaugh and Trussell, 1980). Activated carbon as a treatment for dissolved organics was discussed by Benefield et al, in the publication, " Process Chemistry for Water and Wastewater Treatment " (Benefield et al, 1982).

After 1984, information more directly related to contamination and remediation of USTs appeared. The first addition of Canter and Knox (1985) discussed several technologies available for remediating groundwater. This book gives professionals in the industry the ability to review all available technologies and their effectiveness and application to different contaminants.

In 1988, PEI Associates, Inc., prepared the document, " The Handbook of Underground Storage Tank Safety and Correction Technology ", for EPA's Office of Research and Development, Hazardous Waste Engineering Research Laboratory (PEI Associates Inc., 1988). It addresses transport pathways of released substances, techniques for evaluating the extent of a release, factors influencing risk to human health and the environment, techniques for selecting initial corrective action response technologies and detailed technical profiles of corrective action technologies. In the same year, Roy F. Weston, Inc., (1988) prepared Remedial Technologies for Leaking Underground Storage Tanks, for the Electric Power Research Institute in Washington, D.C. for the electric utility industry, which owns and operates many USTs. Additional research was prepared by D.C. Noonan et al, (1988) addressing selected technologies and Edward Bouwer's article of groundwater remediation (Bouwer et al, August 1988).

Soil venting techniques were researched by Hutzler et al (Jan. 1990) for the EPA and by Paul Johnson et al (1989). Ducreux et al (1990) observed the processes affecting hydrocarbon mobility. Disposal of contaminated soil in Oklahoma was prepared by Dr. Vernon A. Mast (Nov. 1990). Corrective action technologies were discussed by Reidy et al, (June 1990) and Camp Dresser and McKee, Inc. (June 1990).

Biological treatment has been discussed by Morgan and Watkinson (1990), Thomas et al (1990), Huling and Bledsoe (Feb. 1990), and Hutchins et al (1991). The use of surfactants was researched by Abdul et al (Dec. 1990) and by Couillard et al (1991). The fate of benzene and other compounds in gasoline was studied by Hadley et al (Jan.-Feb 1991) in California. The effectiveness of groundwater extraction systems was published by Haley et al (Winter 1991). The Oklahoma Corporation Commission General Rules and Regulations Governing Underground Storage Tanks in Oklahoma (revised 1991) addresses contaminated soil and groundwater in Oklahoma.

### Risk Assessment

The federal government realized benzene to be an occupational exposure to the environment, primarily from gasoline (EPA/440/4-85/006) in January 1982. Human exposure and its danger has been studied by Phillips and Jones (1978), MacFarland et al (1984) and Hadler et al (1986). In 1986, the US Environmental Protection Agency published the <u>Superfund Public Health Evaluation Manual</u>, (USEPA, 1986) giving the accepted methodology for assessing risk. Shamsky and Samimi (1987) and Kramer (1989) calculated risk associated to contractors with USTs. Accepted methodologies for assessing risk to human health and the environment are

explained by Cohrssen and Covello (1989), and the U.S. Environmental Protection Agency (USEPA, March 1989), (USEPA, Dec. 1989).

#### CHAPTER III

## SITE CHARACTERIZATION

#### Introduction

Proper site characterization has been over looked or too often over simplified at many contaminated sites. Leaking underground storage tanks in the United States number in the hundreds of thousands. If proper site characterization of the soil and groundwater is not conducted, the remediation goals will most likely not be achieved. An effective response to a release of petroleum products requires understanding site conditions and defining appropriate remediation goals. These vary from site to site and can range from no immediate action to removal of all petroleum product contamination from the subsurface.

During the site characterization, strong emphasis should be on the logging of soils in borings and monitoring wells. Proper locations of soil borings and monitoring wells is extremely critical for a site characterization that will aid in remedial design. It is important to understand how gasoline from a leaking underground storage tank travels through the subsurface.

#### Contaminant Migration Pathways

Figure 1 (pg. 14) depicts a leak from an underground storage tank to the subsurface (EPA/600/2-90/027). Leakage from underground storage tanks typically occurs into the vadose zone which is the geological profile extending from ground surface to the upper surface of the principal waterbearing formation. The term "vadose zone" is preferable to the often used term "unsaturated zone" because saturated regions are frequently present in the vadose zone (USEPA, June 1987).

During the seepage period through the soil, hydrocarbons move under the influence not only of gravity but also of capillary forces in all directions. A zone develops around the underground storage tank and as in the capillary fringe, the oil saturation decreases in an outward direction. This is called the "oil wetting zone" (See figure 2). In the "oil percolation zone", gravitational forces are dominant.

In passing through the porous media, a residual saturation of gasoline adheres to soil particles. The gasoline held in the residually saturated soil is considered to be relatively immobile (Hoag and Marley, June 1986). Smaller soil particles have a much greater available surface area and greater capillary forces. Increasing moisture content greatly reduces the gasoline retention at residual saturation. If the soil initially contains some residual

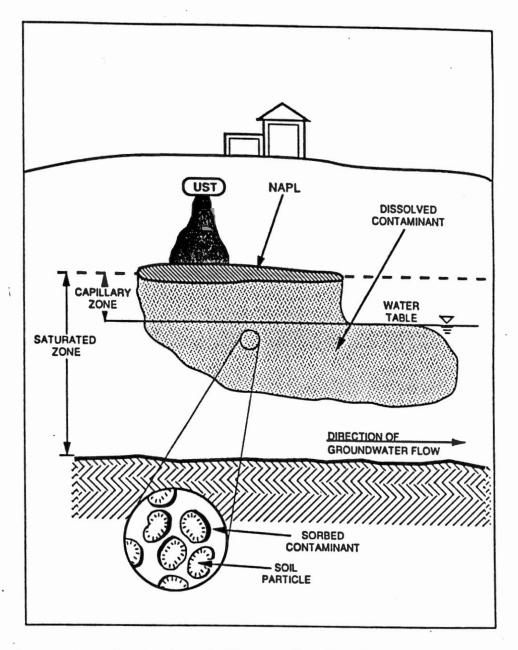


Figure 1. Contaminant Phases in the Saturated Zone (EPA/600/2-90/027, pg. 2)

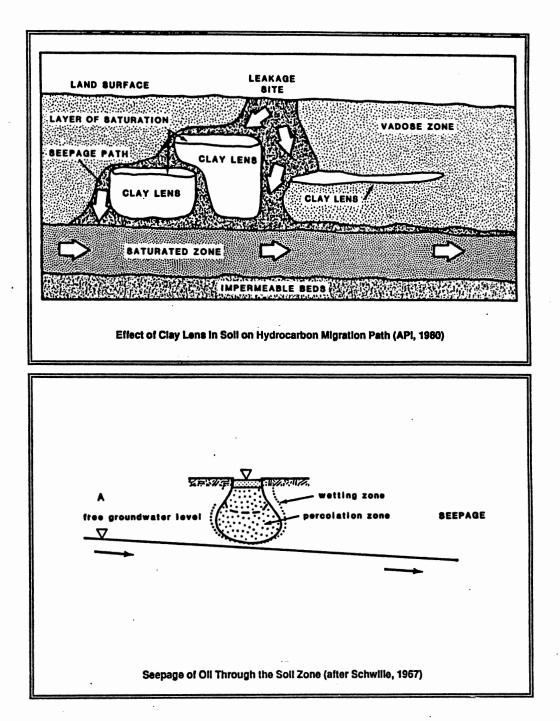


Figure 2. Seepage of Oil Through the Soil Zone (Roy F. Weston, Inc., 1988, pg. 2-4)

water, a three-phase fluid system is formed and the degree of wettability among fluids often decreases in the order of water, organic contaminant and air (Kia and Abdul, July 1990).

At field capacity moisture content, the sand particles are primarily water wet. These actions tend to reduce the overall soil surface area available for contact by the gasoline. Therefore, the retention of organic contaminants in the unsaturated subsurface depends strongly on the relative wettability of the coexisting fluids (Kia and Abdul, July 1990).

The gasoline plume in the subsurface is transported by certain mechanisms. Diffusive transport in the unsaturated zone is a significant transport mechanism which can cause aqueous and vapor plumes to spread away from the immiscible liquid source, resulting in increasing groundwater contaminating potential (Baehr, Oct. 1987). Advection is another major transport mechanism for vapors in the subsurface from leaking underground storage tanks (Carberry and Lee, Oct. 1987).

In the subsurface there exists a partitioning of contaminants between four subsurface phases: the pore-gas, pore-water, solid-sorbed and a nonaqueous liquid phase (Kerfoot, 1991). Vapor transport in the unsaturated zone has an important influence on the fate of volatile organic compounds released into the subsurface (Mendoza and McAlary,

March-April 1990). Natural seasonal changes in the subsurface temperature and moisture contents could result in significant changes in gas-phase concentrations without changes in the total contaminant mass present. The dynamics of volatile organic compounds in unsaturated soils include dissolution to the aqueous phase from the gas phase, volatilization from the aqueous to the gas phase, gaseous diffusion, aqueous diffusion and hydrodynamic dispersion (Cho and Jaffe, 1990).

After reaching the water table, the liquid density determines to a large extent how the NAPL will move vertically in the saturated zone. The denser portion will sink through the aquifer until it reaches the base. From here it will travel under the influence of gravity.( Refer to figure 3)

In most hydrogeologic investigatory programs, crosssections of the soil and geology are conducted as well as groundwater contour maps. This data gives the direction of groundwater flow and aids in plume delineation. Water levelmeasurements are used and when present product thickness is recorded. When plume delineation is conducted, however, little or no emphasis is placed on the capillary fringe and its affect on the true vertical profile or its true product thickness in the water-table aquifer. Though many theories have been proposed over the true product thickness, variation between theories, should not inhibit true site

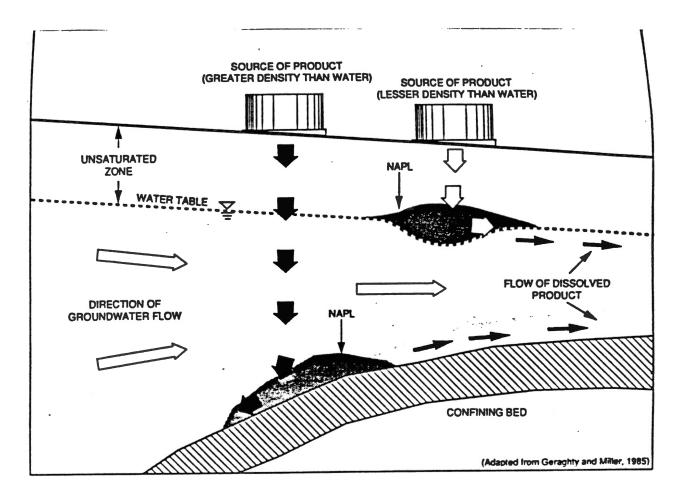


Figure 3. The Effect of Density on Contaminant Plume Migration (EPA/600/2-90/027, June 1990, pg. 41)

characterization. It is not necessary to develop new or more expensive technologies to characterize sites where leaking underground storage tanks containing gasoline or other Light Non Aqueous Phase Liquids (LNAPL's) have been released into the environment. During soil and groundwater analysis programs, it is important to have proper soil logging conducted by knowledgeable professionals.

#### Soil

A soil sampling and analysis program should be conducted at the investigated site. All soil borings should be conducted with decontaminated equipment. The most commonly used method is hollow-stem auger drilling. Initially each boring is drilled through concrete or whatever type of cover is present at the site. Next a decontaminated 18 inch (or 24 inch) split spoon is hammered into the soil for a soil sample to be recovered. The soil sample is logged by describing its color, moisture, density, stiffness and any other characteristic beneficial to proper soil classification. Next, record the depth the sample was taken from and the soil type classification according to the Unified Soil Classification System ( USCS ). An example boring log is given in figure 4. Screening of the soil samples should be conducted with the use of a photoionization detector (PID) or a flame ionization detector (FID). The reading should be recorded on the soil

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LOG	OF	SOIL	BORING	DRILLER			ROJECT		B	BORING SB - 1					
		Faul	Ironmentel	DRILL METHODNob11e SAMPLE METHOD SS			.IENT			و.	PAGE OF				
		Cor	nsultants	SAMPLE METHOD BOREHOLE DIAME		LO	CATION		JC	JOB Ne.					
				ELEVATION	R/A	무	TE START			LC	OGED				
				OTHER		TI	TË END				ECKED				
P	ID	OR, MOISTURE	SOIL DESCRI	PTION	SOIL	DEPTH	  BLOWS/0"		DRIVEN		TYPE	ADDNL INFO			
	•+-			·		+									
F 1						Ę۱									
2			inge, moist,	medium		t 2				•					
- 3	•	tiff, si	lty clay			× 3	4,4,4	1	18	10	SS				
F ]					-	F.				ŀ					
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<b>Z</b> 7	G	ray/oran	ige, moist, v	ery stiff,		ţ,									
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			lt. brown, S lty sand No.			<b>9</b>									
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	5	ray, sat	bove, gradin urated, loos	e silty san		x	4,2,8	7	18	10	ss				
					• •	•			••						

Figure 4. Log of Soil Boring

boring log according to the proper depth interval. After logging of the soil sample, the soil is placed in a glass jar with a teflon lid and labeled accordingly. After split spoon sampling, the sampled interval is drilled with a hollow stem auger to the next sampling depth. This cycle of split spoon sampling followed by drilling continues until the total depth of the soil boring is reached.

During the split spoon sampling process, it is critical to fill the sample jar as much as possible to theoretically leave "no headspace" in the jar. This is very important since in the laboratory, the hydrocarbon vapors will escape when the sample jar is opened for gas chromatography (GC) analysis.

After filling the soil jars with no headspace, tape the lid around the jar to insure sample integrity. Then preserve according to the laboratories specifications, most likely, ice. After obtaining the soil sample for laboratory analysis, place more soil from the 18 inch split spoon into a second jar with headspace and seal with plastic or aluminum foil. Set the soil sample jar in the sunlight at 70 F for thirty (30) minutes. This will help any available volatiles to concentrate. Next insert the probe of the PID or FID through the foil and observe the reading. Record the highest reading observed. Be sure to calibrate the PID before screening another soil sample. During the soil sampling process, a cooler with ice can be used to preserve

the soil samples until delivery to an accredited laboratory for Total Petroleum Hydrocarbons (TPH) and benzene, toluene, ethylbenzene and xylene (BTEX) analysis.

A Chain of Custody (COC) record should be provided for all samples obtained for analysis. Figure 5 is a copy of a chain of custody record used at an investigated site. The purpose of the Chain of Custody (COC) record is to provide written documentation that all samples developed are properly handled within Quality Assurance and Quality Control (QA/QC) procedures. In this record, all persons in possession of the soil samples listed on the record sign for receipt and release of the samples, thus providing sample integrity.

If possible, several or all samples with hydrocarbons detected by the PID in each borehole should be sent to the laboratory. This method, however, is not economical and most likely the soil sample sent to the analytical laboratory is the one with the highest level detected by the PID. If none of the samples obtained in a boring give an indication of hydrocarbons, then the soil sample at the water table should be the one selected for analysis. This sample is determined by its saturation. Gasoline, if present, should be at the top of the capillary fringe, which is above 100% water saturation in the soil.

-		
	Client/Job No:	
	Job Name:	

CHAIN OF CUSTODY RECORD											
Sample No.	Lab LD. No.	Date	Time	Matrix	No. of Containers	Analysis Req	uested/Remarks				
5B-7B		8-3/-89	—	5016	1	TPH,	<i>Β</i> τχ·				
5B-8A		8-31-89		SOIL	1	TPH,	ΒΤΧ				
53-8B		8-31-89	-	5016	1	TPH,	BTX				
5B-9A		9-1-89		SOIL	1	TP#,	BTX				
58-93		9-1-89		SorL	1	TPH,	BTX				
Comments	· <u>*</u>	1 less	e tu Frid	maron	and re	alone con	wersation				
		Thank	Date: 9- Time: 18		pment Metho	d:	. <i>K</i>				
Received by:         State:         9-5-89         Relinquished by:         Date:         Date:           Time:         1800         HRS         Time:											
Received by: Received by: Date: 9-6-59 Relinquished by: Date: Date: Time: 8:15											
Final Disposition of Samples:											
Received	Received by: Date: Time:										

Pink, Field Copy - Yellow, Lab Copy - White, Original - To be returned with results.

Figure 5. Chain of Custody Record

•

All soil samples should be analyzed by an EPA accredited laboratory for Total Petroleum Hydrocarbons (TPH), using EPA method 418.1 (IR) and for Benzene, Toluene, Ethylbenzene and Xylene (BTEX) using EPA Method 602 (modified to include xylene).

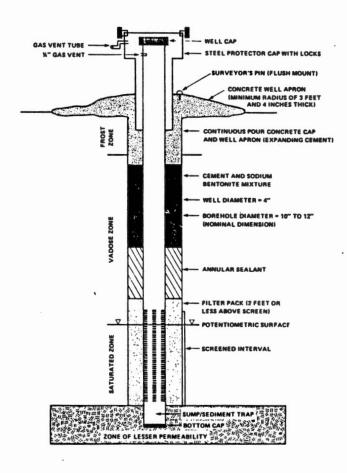
Once analytical results are available, determination of the extent of contamination is possible. Using the analytical results and the surveyed soil boring locations, a soil contamination contour map can be developed. A Plan view, two dimensional map has been the preferred method. This method however assumes the same vertical depth of contamination in all the borings. This is where a more detailed delineation of the plume need be conducted. A three dimensional drawing should be constructed showing a crosssectional view and understanding of the subsurface soils and conditions at a site. A stratigraphic cross-section of the soils need to be correlated between borings. This is critical in the location of monitoring wells for proper plume delineation in the local groundwater.

## Groundwater

Groundwater contamination by leaking underground storage tanks is the most serious problem encountered when assessing a site. Once the soil sampling analysis has been conducted, it is possible to determine the need for a groundwater analysis. If groundwater contamination is suspected, a groundwater analysis program should be implemented. The location of the groundwater monitoring wells is based on: (1) location of source, (2) maximum soil contamination and, (3) any data or information indicating a specific location as a potential source.

During the installation of monitoring wells, proper design and construction is extremely important. Figure 6 is a diagram of a standard overburden groundwater monitoring well.

Several water well-drilling methods are available for the installation of groundwater monitoring wells. It is important that the drilling method or methods used minimize disturbance of subsurface materials and not contaminate the subsurface and groundwater (40 CFR 265.91 (c)). Drilling method selections are based on site-specific geologic conditions. Drilling methods available are: (1) air rotary, (2) water/mud rotary, (3) cable tool, (4) hollow stem continuous auger and (5) solid stem continuous auger (NWWA, September 1986). It is important that regardless of the drilling method selected, the drilling equipment should be decontaminated. The decontamination procedure should be conducted before use and between monitoring wells to prevent cross contamination of wells where contamination is suspected or where contamination has been detected. The most common method of decontamination is with a pressure washer. Be sure contaminated rinsate is collected and disposed.



GENERAL MONITORING WELL - CROSS SECTION

# Figure 6.

 Standard Groundwater Monitoring Well (NWWA, Sept. 1986, pg. 79)

During the drilling of a monitoring well, it is important to log the soils as previously described. This gives additional information to the contaminated site. Upon reaching saturated soils, it is critical to note any free product as well as readings from a volatile organic analyzer. If possible, a monitoring well should be drilled to a total depth that penetrates the entire aquifer (i.e. until an impermeable boundary is encountered). This will be beneficial during a pumping test to accurately determine the transmissity and hydraulic conductivity of the aquifer. A sample of aquifer material should be obtained for sieve analysis to insure the engineer's field classification. If the free product is encountered, sampling methods for the determination of residual gasoline content in the contaminated capillary fringe should be conducted.

A new method consisting of laboratory partitioning of intact stainless steel core sleeves versus field extrusion of core barrels has been conducted. The barrel extrusion sampling method yielded a vertical profile with 0.10m resolution over an essentially continuous 5.0m interval from the ground surface to the water table. The sleeve segment alternative yielded a more resolved 0.03m vertical profile over a shorter 0.8m interval through the capillary fringe. (Ostendorf et al, Spring 1991). Core barrel extrusion into pint-size Mason jars is relatively rapid and is the method of choice for vertically integrated data.

After drilling the bore hole for a monitoring well, it is critical to use well construction materials that are durable enough to resist chemical and physical degradation and do not interfere with the quality of ground-water samples. Specific well components that are of concern include well casings, well screens, filter packs and annular seals or backfills.

The materials used to construct the filter pack of a monitoring well, should be chemically inert, well rounded and dimensionally stable. Generally, coarse sand is used, although natural gravel packs are acceptable, as long as a sieve analysis is conducted to establish the appropriate well screen slot size and a chemical inertness of the natural soil. After filling the annular space at least two (2) feet above the screened interval, a sealant must be placed. The preferred sealant is sodium bentonite. The materials used to seal the annular space must prevent the migration of contaminants to the sampling zone from the surface or intermediate zones and prevent cross contamination between strata. From the bentonite seal to the ground surface, an expanding cement grout should fill annular space.

Upon completion of the well, installation of a suitable threaded, flanged or compression seal should be used to prevent either tampering with the well or the entrance of foreign material into it.

After construction of a monitoring well, it is necessary to develop the well prior to groundwater sampling or water level measurements. A variety of techniques exist for developing a monitoring well. Effective development requires reversals or surges in flow to avoid bridging by particles. These reversals or surges can be created by using surge blocks, bailers or pumps. The most common technique is with a submersible pump. The well should be pumped until the discharge of groundwater is as clay and silt free as possible. A well design construction diagram should be drawn to reflect proper design. All monitoring wells should be surveyed and the casing height should be measured by a licensed surveyor to an accuracy of 0.01 foot. Sometimes the placement of a topographic benchmark on the investigated site is required. A survey mark should be placed on the casing of all wells for use as a measuring point.

Water level measurements should be collected within a 24 hour period. The reasons for this practice are:

-tidally influenced aquifer:

-aquifers affected by river stage, impoundments, and/or unlined ditches;

-aquifers stressed by intermittent pumping of production wells;

-aquifers being actively recharged due to a precipitation event. (NWWA, September 1986)

If "free" or "floating" product is found, water level measurements should be adjusted to reflect its true elevation. An interface probe should be used in this case and product thickness recorded, so a true product thickness in the formation can be calculated. The adjustment of the water level due to floating product and the actual product thickness in the formation can be calculated using the equation shown below:

ACT = APT -  $(D_{WT} + Hm)$ 

ACT	-	Actual thickness in formation
APT	-	Apparent product thickness (measured)
$D_{wT}$	-	Depressed water table
Hm	-	Height of capillary fringe

Hm = function of media

<u>media</u>	<u> </u>
coarse sand	1 - 2"
medium sand	4 - 14"
fine sand	14 - 27"
silt	27 - 59"
clay	78 - 160"

A minimum of three (3) groundwater monitoring wells must be used to develop a potentiometric surface map. A potentiometric surface or water-level map is a graphical representation of the gradient. The hydraulic gradient is the driving force that causes ground water to move in the direction of maximum head decrease. Potentiometric surface maps are an essential part of any groundwater investigation because they indicate the direction in which groundwater is moving and provide an estimate of the gradient, which controls velocity (EPA/625/6-87/016).

Characterization of the groundwater, now requires obtaining groundwater samples and having them analyzed by an accredited laboratory using approved EPA methods. In order to obtain a representative groundwater sample for analysis, the volume of groundwater in each well should be calculated. The depth to water, total depth and well diameter are needed. Once the well volume has been calculated, the volume of groundwater removed must be equal to or greater than three (3) well volumes. Only fluorocarbon resin or stainless steel sampling devices should be used. Also there must be dedicated samplers for each well, if not, the operator should thoroughly clean the sampler between samples, as well as take blank samples to ensure integrity. Bailers are the most commonly used groundwater sampling devices.

Sample containers should match the studied contaminant. Appendix A gives the recommended container, preservative, maximum holding time and minimum volume required for analysis. For gasoline contamination from leaking underground storage tanks, no headspace should exist in the sample containers to minimize the possibility of volatilization of organics. Field logs and laboratory analysis reports should note the headspace in the sample container(s) at the time of receipt by the laboratory, as well as at the time the sample was first transferred to the sample container at the wellhead. A Chain of Custody form should be used with all samples, soil and groundwater. A Chain of Custody record is to provide written documentation that all the samples obtained are properly handled with in Quality Assurance and Quality Control procedures (QA\QC). In this record, all persons in possession of the samples listed on the record sign for receipt and release of the samples, thus providing sample integrity.

With the results of the laboratory analyses it is possible to determine the vertical and horizontal concentration profiles of all the hazardous waste constituents in the hydrocarbon plume(s) escaping from the leaking underground storage tank(s). In addition, the rate and extent of contaminant migration must be established. Since the NAPL and dissolved contaminant can move at different rates and in different directions in the subsurface, the two (2) phases may need to be delineated separately.

Fate and transport of gasoline contaminants can be estimated using different techniques. Much attention has been given to groundwater models. The most effective manner to understand the hydrologic characteristics of the contaminated aquifer is through conducting a pumping test. Pumping tests provide several types of information to the hydrogeologist, such as conditions within, and in the immediate vicinity of the pumping well, the large-scale flow

behavior in the system (e.g., the nature of the vertical and lateral boundaries), and estimates of the transmissive and storage properties of the aquifer (Butler, May-June 1990). Through this technique, aquifer characteristics that are site specific are obtained. When the transmissity and hydraulic conductivity of an aquifer is known, a more accurate determination of the transport of the contaminant is known. Once the total vertical and horizontal extent of the contaminant is known, as well as the groundwater characteristics, a proper remedial design can be implemented.

#### CHAPTER IV

## REMEDIATION

## Introduction

There are several technologies available for the cleanup of soils and groundwater contaminated by leaking underground storage tanks. After a release has been evaluated, appropriate corrective actions should begin immediately. It is essential that early discovery and containment of any suspected leak occur as soon as possible so that recovery procedures may be initiated and the influence of any release can be minimized. Normally, the first action taken is initial abatement procedures (Okla. Corp. Comm., 1991).

The release should be reported to the State UST regulatory agency as required by telephone or electronic mail. Remove as much of any remaining product from the leaking UST to prevent further release to the environment. Next, monitor and mitigate any imminent and immediate risk to human health and the environment. Some hazards include vapors or free product that have migrated off-site. Remove as much free product as possible, repair or remove the leaking tank and restrict access to the site.

Figure 7 presents a listing of options available for the initial response to typical UST release situations (PEI Assoc. Inc., 1988).

A remediation plan will vary from site to site depending on the site specific conditions encountered during the initial abatement procedures and the site characterization. Selecting and implementing a remedial method depends first of all on a determination of cleanup goals, which are the contaminant levels or concentration limits to which the site must be cleaned. These are usually based on either an assessment of potential risk or regulatory standards. Next the remedial plan is chosen by assessing the feasibility of each option to achieve the desired cleanup goal, the acceptability of the method and evaluating the economics. The method selected may not always be the most cost effective.

In setting remediation goals an effective remediation plan must adequately address all phases of a cleanup. Returning a site to pre-release conditions is desirable, but not all sites will require such goals. The approach to a remediation plan can be put into three broad categories: 1) no active remediation; 2) containment of subsurface contaminants; and 3) treatment and/or removal of contaminants at the site (EPA/600/2-90/027).

Situation	Tank repair/removal	Free product recovery	Ground-water recovery and treatment	Subsurface barriers	Soil excavation	Vapor migration control and collection	Sediment removal	Surface water diversion drainage	Alternative/treatment central water supply	Alternative/treatment point-of-use water supply	Restoration of utility, water, and sewer lines	Evacuation of nearby residents	Restricted egress/ingress
Ground-water contamination													
Existing public or private wells Potential future source of water supply Hydrologic connection to surface water	•	•	•	•	•								
Soli contamination												.	
Potential for direct human contact: nuisance or health hazard Agricultural use Potential source of future releases to ground water	•	•	•	•	•	•	•	•		•			
Surface-water contamination										1			
Drinking water supply Source or irrigation water Water-contact recreation Commercial or sport fishing Ecological habitat	• • • •	•		•				•	•	•	•		•
Other hazards	Į .												1
Danger of fire or explosion Property damage to nearby dwellings Vapors in dwellings	•		e.			•						•	•

Figure 7. Potential Initial Response Situations and Corrective Actions (PEI Assoc. Inc., 1988, pg. 4-6)

This report has divided remedial alternatives for leaking underground storage tanks into three categories: 1) physical control measures; 2) treatment of contaminated soils; 3)and treatment of contaminated groundwater. Chapter four (4) will discuss all three categories in general terms. It is important to reiterate that conditions will vary from site to site and each remediation plan for a leaking UST is site specific.

#### Physical Control Measures

Physical control measures are utilized for preventing and/or minimizing the pollution of groundwater for many contaminants. These measures are applicable to sites with leaking underground storage tanks needing initial abatement procedures and/or in conjunction with soil and groundwater remedial actions. This section discusses six distinctive physical control measures: 1) source control,

2) solidification, 3) well systems, 4) interceptor systems,5) subsurface barriers, 6) and surface capping and liners.

#### Source control

Source control attempts to minimize and/or prevent soil and groundwater prevention before a release occurs. For UST's, source control includes removing the product from a tank before a release and if abandonment is considered or after a release to minimize subsurface contamination.

During excavation of contaminated soil, the use of polyethylene sheeting beneath and covering the soil is source control from wind and precipitation spreading gasoline to the environment. The advantage of source control is its reduction of threat from a hazard to the environment. The disadvantages of source control strategies are the increase in short term capital and maintenance costs.

### Solidification

Solidification is a process by which a solid matrix is created of the waste. For leaking underground storage tanks, the product, its bottom sludge and the contaminated soil can be solidified and thereby immobilized. Types of solidification include: 1) cement addition; 2) lime addition; 3) embedding in thermoplastic materials such as bitumen, paraffin or polyethylene; 4) addition on an organic polymer; 5) encapsulation in an inert coating; 6) and the formation of a glass by fusion with silica (Canter and Knox, 1985). Unless metals such as lead are present, solidification is not a feasible physical control measure due to its high cost.

#### Well systems

Well systems are presently the most common method of groundwater pollution control for leaking UST systems. Free product provides a strong economic incentive for remediation since the product recovered can be utilized. This has lead considerable work to be directed toward developing hydrocarbon recovery systems.

Well systems are used to 1) control the migration of a contaminant from leaving a site (pressure ridge system), and posing a hazard to human health and the environment or 2) to control the hydrologic gradient of groundwater to flow to recovery wells where the contaminated groundwater can be recovered and either treated or disposed. The control of groundwater flow and its direction is known as " plume management ".

Four design options are available for hydrocarbon recovery systems: 1) single-pump systems using one recovery well, 2) single-pump systems utilizing multiple wells, 3) two-pump systems utilizing two or more recovery wells, and 4) two-pump systems utilizing one recovery well (Canter and Knox, 1985).

The single-pump system has the advantage of lower costs in equipment. However the disadvantage is that this system produces an oil-water mix requiring its separation on the surface with an oil-water separator. Additional space for remedial equipment is required on the surface and some sites may not have the space. The two-pump system has the advantage of creating a lowering of the water table by the lower pump while the upper pump skims the hydrocarbon from the upper most portion of the aquifer. The disadvantage of the two pump system is its higher cost and this cost multiplies by each additional recovery well added to the remedial plan. In addition, the two pump system has higher drilling cost for the recovery well since a larger diameter is necessary to house two pumps.

Well systems need the information obtained from the site characterization, especially the aquifer characteristics; transmissivity (T), hydraulic conductivity (K), and groundwater velocity (Driscoll, 1987). This data is best obtained from pumping tests, since they are site specific. Pumping tests also provide information identifying heterogeneities, no flow boundaries or recharge zones. The most important information obtained from a pumping test is determining the radius of influence of the recovery well. With the radius of influence, a minimum number of recovery wells can be strategically placed over the contaminated site. This method is the most effective and the most economic, by reducing the number of unnecessary recovery wells, the pump systems maintenance and surveillance of the system.

In the absence of pumping tests data, the radius of influence can be estimated using the following equations for an aquifer in equilibrium, homogeneous and isotropic (Canter and Knox, 1985).

For a confined aquifer,  $\ln Ro = \frac{T(H-hw) + \ln rw}{229 Q}$ . For an unconfined aquifer,  $\ln Ro = \frac{K(H^2 - hw^2) + \ln rw}{458 Q}$ ,

where:

T = Transmissivity (gpd/ft), K = hydraulic conductivity (gpd/ft<sup>2</sup>), Ro = radius of influence (ft), H = total head (ft) before pumping, hw = head in well (ft), Q = Pumping rate (gpm), and rw = well radius (ft).

When using these equations, it must be understood that the radius of influence is only an estimate so when designing well spacing a safety factor should be used:

R design = 0.7Ro

#### Interceptor systems

Interceptor systems require the evacuation of a trench below the water table in order to trap contaminated groundwater. Compared to well systems, interceptor systems do not control the groundwater gradient and direction of flow. In order to use an intercept system it is necessary to know the direction of groundwater flow in relation to the

zone of contamination or the source of release. The trench must be placed downgradient of the plume in order to intercept. The trench or subsurface drain functions similarly to an infinite line of extraction wells by giving the effect of a continuous zone of depression which runs the length of the trench. Usually the trench is filled with perforated pipe and coarse back fill material and is sloped to a sump where the collected groundwater can be pumped to the surface to be treated or disposed. The most obvious advantage of interceptor systems is their relatively simple construction methods. Interceptor systems have the advantage over well systems at a site where the permeability of the soil is low and groundwater flow is slow so that it is not technically feasible to install recovery wells with small radii of influence. Disadvantages include the danger of dissolved contaminants seeping past the trenches and the danger posed by the open system to fires or explosions.

## Subsurface barriers

A subsurface barrier is a physical control measure used to either contain a contaminant plume from leaving a site or to keep a contaminant from entering a clean up site, groundwater wells, streams, or any other environment that would pose a threat to human health and the environment. Three types of subsurface barriers are sheet piling, grouting and slurry walls.

Sheet piling consists of driving lengths of steel connecting together in the ground to form an impermeable barrier to groundwater flow. A pile hammer is used to drive sections of steel sheeting into the ground. Initially the sheet piling barrier is not totally impermeable, but as time passes groundwater carrying fine particles will clog and close these gaps. Steel sheet piling can be considered permanent because experience has show that corrosion is not a factor in causing failures (Canter and Knox, 1985).

Grouting is a more common method of subsurface barriers due to its wide diversity of hazardous materials it can effectively contain. Initially a site's soil must be properly characterized for a good design. When designed on the basis of thorough preliminary investigations, grouts can be very successful. Grouting consists of injecting a liquid, slurry or emulsion under pressure into the soil. This flows into void spaces in the soil and solidifies, reducing the hydraulic conductivity and increasing the soil-bearing capacity. There are two classifications of grouts, particulate and chemical. Particulate grout consists of water plus particulates phases which set in the subsurface. Chemical grouts consist of injecting two or more liquids which set when they come in contact. Different techniques for grout installation are stage, packer and the driven-rod methods.

Slurry walls are similar to grouting, except a trench is dug and backfilled with an impermeable material. These walls can be placed upgradient to prevent groundwater flow to a site or placed downgradient to prevent flow of contaminated water from a site. The backfill material can either be a soil-bentonite mixture or a cement-bentonite mixture.

## Surface Cappping and Liners

Surficial capping and liners have been used for many years to control leachates from waste sites and are applicable to sites where leaking underground storage tanks have contaminated the subsurface. Capping is used to minimize the infiltration of water into contaminated soil so that the contaminant is not leached into the groundwater. An impermeable liner is used to contain contaminants from spreading and are usually used in combination with a leachable collection systems. Depending on the degree of clean-up required, capping and liners will keep minor amounts of hydrocarbons bound to soil particles from becoming a threat to human health and the environment.

#### Treatment of Contaminated Soil

The treatment of contaminated soil by leaking UST's is different for each site due to site specific conditions. Important factors that contribute to the corrective action plan are the amount of contaminated soil, the contaminant level, the clean up goals, and the cost for each treatment. Treatments for gasoline contaminated soil have been divided into six categories: 1) excavation and disposal, 2) landfarming/enhanced volatilization, 3) incineration, 4) soil vapor extraction, 5) soil washing/extraction, and 6) microbial degradation.

# Excavation and Disposal

The most common practice today for gasoline contaminated soil is excavation and disposal. Disposal of the contaminated soil depends on the state regulatory agency, the amount of liability the generator wants to accept and the cost of disposal. In Oklahoma, gasoline contaminated soil is considered a non-hazardous industrial waste and can be landfilled in many available landfills (Mast, Nov. 1990). Appendix B is a list of landfills in Oklahoma that accept gasoline contaminated soil. Before these soils can be landfilled, composite samples are obtained and analyzed for: 1) Total Petroleum Hydrocarbons (TPH), must be <500 mg/kg; 2) Benzene, Toluene, Xylene (BTX); 3) Total lead and/or E.P. Toxicity for lead, and 4) any RCRA listed materials (Mast, Nov. 1990).

Next, a permit for approval of disposal of the soil must be obtained. Once approved, state licensed transportation is required to deliver the contaminated soils to the landfill. This is the most cost-effective manner in Oklahoma as long as the amount of contaminated soil does not exceed the cost of other options that will be discussed in this chapter.

The advantage of excavation and disposal of soils containing hydrocarbons is the opportunity for rapid and complete site cleanup. Another advantage is the effectiveness of site cleanup because it can be confirmed by field sampling and laboratory analyses that all the petroleum-laden soils have been removed. (Roy F. Weston Inc., 1988). The disadvantages of excavation and disposal without treatment is the liability in transportation and disposal the generator is incurring. Unless aerobic conditions exists until total degradation of the gasoline, the disposer can be held accountable for environmental problems that may occur in the future. By disposing in a municipal or privately operated landfill, the generator has no control over and must accept the landfill operator's promise to maintain environmentally sound operating practices.

Landfilling costs vary with the type and toxicity of the waste and the disposal site. Industrial wastes can be

landfilled for \$40.00 to \$85.00/ton. Ignitable wastes average about \$125.00/ton. Fees for highly toxic wastes are about \$245.00/ton (EPA 1985a). These fees are in addition to transportation costs, averaging \$3/mile per load (PEI Assoc. Inc., 1988).

#### Landfarming/ Enhanced Volatilization

Landfarming is the process by which soils contaminated by gasoline are removed and spread over an area where naturally-occurring processes are enhanced. These natural processes include volatilization, aeration, biodegradation and photolysis (Roy F. Weston Inc., 1988). If properly performed, landfarming is an effective method for the removal of hydrocarbons from contaminated soils, however, considerable amounts of land and time are required

for total hydrocarbon degradation.

Enhanced volatilization is a process that removes volatile organics from soil by placing contaminated soils in direct contact with clean air to enhance the transfer of contaminants from the soil into the air stream. The air stream is then treated to reduce air emission contaminants. Different methods to enhance volatilization are: mechanical rototilling, enclosed mechanical aeration systems, low temperature thermal stripping systems and pneumatic conveyer systems (EPA/530/UST-88/001). Mechanical rototilling is the process of turning over soils at shallow depths to increase the rate of volatilization. The number of passes required for sufficient volatilization depends on the degree of contamination. The soils moisture content and to a large degree, the weather. Volatilization is best when the weather is hot and the humidity is low.

An enclosed mechanical aeration system is a process by which contaminated soils are mixed in a pugmill or a rotary drum. The volatile components of gasoline are released by the increased air/soil contact caused by the churning action. An induced airflow in the chamber removes the gasoline vapors and filters them through an air pollution control device. Next, the vapors are discharged through a properly sized stack (Mast, Nov. 1990).

Low temperature thermal stripping systems are similar to the enclosed mechanical aeration system described above. The difference is allowing the soil to come in direct contact with a heated screw-auger device or a rotary drum. The desorbed volatile organics/air mixture are routed through an after burner where the organic contaminants are destroyed before being discharged through a properly sized stack.

Pneumatic conveyor systems consist of tubes or ducts to carry air, an induced draft fan, a suitable feeder to disperse particulate solids into the air stream and a

cyclone collector or another type of separation equipment to recover the solids from the gas stream (EPA/530/UST-88/001). The inlet air is heated by several units to 300'F for volatilization of organic contaminants.

Documentation exists to support low temperature thermal stripping systems to be most effective in removing gasoline constituents (i.e., compounds with high vapor pressures) from soil.

### Incineration

Incineration is a complete destruction technology to effectively eliminate gasoline from soils by complete oxidation. Contaminated soil is added to a high-temperature combustion chamber (rotary kiln, fixed hearth, multiple hearth, fluidized bed, liquid combustion chamber, etc.) where the organic compounds are burned and converted to carbon dioxide, water and acid gases (Mast, Nov. 1990). These high-temperature combustion chambers achieve destruction and removal efficiencies (DRE) of 99.99 percent or greater as required by RCRA for hazardous wastes.

Rotating kiln and fluidized bed incinerators are available as transportable units for on-site soils processing and as large-scale commercial facilities (Roy F. Weston Inc., 1988). Use of mobile units are limited by permitting processes for emissions, which may take considerable time and is expensive. Costs for incineration vary depending on the particular characteristics of the soil and waste. CDM (1986) conducted a survey, prices ranged from \$150.00 to \$480.00/ton (\$200.00 to \$640.00/yd.<sup>3</sup>) for incineration of 20,000 yd.<sup>3</sup> of hypothetical hazardous waste. (EPA/530/UST-88/001)

### Soil Vapor Extraction

Soil vapor extraction is an in situ process by which volatile organic chemicals (VOCs) are removed from subsurface soils by mechanically drawing or venting air through the soil matrix (Mast, Nov. 1990). This process consists of vents of various designs with gravel packs extending to the soil surface or slotted/unslotted well casings installed with or without a gravel pack. Any other configuration in design may be used that allows gases to move from the soil.

There are two systems for vapor extraction: 1) passive and 2) active. Passive systems have vents that are open to the atmosphere and do not require energy for the extraction of vapors. Active systems use pressure or vacuum pumps to accelerate the removal of gasoline vapors from the soil. With pressurized venting, air is forced into the soil by an infiltrating vent. In vacuum venting, the vacuum is created by the extraction well removing the vapors. Pressure and vacuum systems could be used in tandem to increase the rate at which gasoline is removed from a site (EPA/530/UST-88/001).

Soil vapor extraction can be effectively used for removing a wide range of volatile chemicals over a wide range of conditions. The efficiency of any soil venting operation will depend significantly on three factors: vapor flow rate, vapor flow path relative to the contaminant distribution and composition of the contaminant ( Johnson et al, 1989).

The advantages of soil vapor extraction is that it minimally disturbs the contaminated soil, it can be constructed from standard equipment, it can be used to treat larger volumes of soil that can be practically excavated, and it has the potential for product recovery (EPA/600/52-89/024).

The limitations of venting are the soil characteristics that impede free movement of vapors to the extraction well, emissions of volitiles and explosion hazards.

## Soil Washing/Extraction

Soil washing is a process by which gasoline is removed from the soil matrix by actively leaching the organic contaminants from the soil into the leaching medium. Then the extracted contaminants in the washing fluid can be removed by conventional treatment methods. Soil washing can be accomplished either in situ as a water flushing system or

processed through a countercurrent extractor system.

The slurry of soil and washing fluid is dewatered by conventional techniques such as sedimentation, filtration, evaporation, dissolved air flotation, or drying beds (EPA/530/UST-88/001). This first process focuses on the extraction of heavy oils from their particle support (clay, silt, sand) with hot water. Two goals of this process is to clean the soil to acceptable levels and to recover oil for energy generation (Couillard et al, 1991). To enhance the soil washing/extraction process studies of surfactants for additives have been performed. In one study, four groups of commercial surfactants were analyzed: 1) ethoxylated alcohols (nonionic), 2) ethoxylated nonylphenols (nonionic), 3) sulfates (anionic) and 4) sulforates (anionic) (Abdul et al, Nov.-Dec. 1990). The conclusion selected Witconol SN 70 (alcohol ethoxylate) as best because it had the lowest critical micelle concentration, the best detergency and solubilization potential and caused the least soil dispersion. Other factors in the selection include: 1) specific gravity of 0.98, keeping the solution in the upper water table with LNAPLs; 2) its lower molecular weight could enhance its movement through soil or aquifer systems; 3) and its viscosity is not expected to adversely affect the flow of the solution through soil or aquifer systems (Abdul et al, Nov.-Dec. 1990).

The effectiveness of surfactants in soil washing extraction was further studied in a research by J. Ducreux, et al in 1990. It was found that the use of surfactants greatly enhances the oil recovery of soluble hydrocarbons with a pre-flush treatment of 10 g/l of NaCl. The sodium cation for calcium cation exchange with the pre-flush treatment reduced the absorption of the surfactant to the soil particles, especially clay and silt. (Ducreux et al, 1990).

Costs of this process is difficult to access since it is a new technology and its use has been limited. However, MTA Remedial Resources, Inc., which has developed a commercial soil washing process, report processing cost of about \$100.00/ton for both capital amortization and operating costs. This cost does not include excavation and disposal. Resource Conservation Co. has estimated a processing cost of about \$120.00/ wet ton. This cost does not include excavation or disposal expense (EPA/530/UST-88/001).

## Microbial Degradation

Microbial degradation is a process where the microorganisms harbored in the soil degrade hydrocarbons and other environmental contaminants. Soil bacteria, actinomycetes and other microbes have been shown to acclimate readily to hydrocarbons in their metabolic

processes to convert them to microbial biomass and carbon dioxide (EPA/530/UST-88/001). Bioremediation can be used to degrade gasoline contaminated soil in situ, or non in situ (land farming, bioreactor or other wise modified environments). Gasoline compounds in the alkane group ( $C_5$  to  $C_{10}$  range) have been shown to biodegrade in the soil environment so long as inhibiting factors do not exist. According to Brookman et al, (1985b), factors affecting the rate of degradation include: 1) indigenous soil microbial population, 2) hydrocarbon type and concentration, 3) soil extraction, expressed as pH, 4) nutrient availability, 5) temperature, 6) moisture content and 7) oxygen content.

The enhancement of biological degradation has been studied by researchers and the addition of hydrogen peroxide, nitrate and oxygen is reviewed. The effect of nitrate addition on a fuel contaminated aquifer was studied by S.R. Hutchins, et al (1991). Nitrate results in anaerobic biodegradation of organic compounds and was less expensive and more soluble than oxygen. Enhanced removals of toluene, ethylbenzene and m, p-xylene were observed with o-xylene being more recalcitrant (Hutchins et al, 1991). Benzene has been found to easily biodegrade under aerobic conditions and is largely dependant on the availability of an adequate supply of oxygen. This was interesting since the most watersoluble constituent of gasoline is benzene (Hadley and Armtrong, Jan.-Feb. 1991). Philip Morgan and Robert Watkinson (1990) assessed three hydrocarbon-contaminated sites for in situ biotreatment and concluded that bioremediation was a feasible treatment. The use of hydrogen peroxide was studied in Granger, India by J.M. Thomas, et al (1990) and the results indicated that the subsurface microflora was active at the site and after being stimulated by hydrogen peroxide, the biodegradation potential remained for 2 years after the process had terminated.

The U.S. EPA in Ada,Oklahoma conducted a laboratory and field study of hydrogen peroxide as an enhancement to bioremediation in Feb. 1990 and the results were conclusive. Hydrogen peroxide decomposes ideally yielding one mole of water and one mole of oxygen. However, a field study at Traverse City, Michigan, indicated that a significant amount of oxygen was lost from the system and was not available for the bioremediation of hydrocarbons. The hydrogen peroxide decomposition resulted in the liberation of oxygen at a rate faster than oxygen could be utilized biologically and solubilized into the aqueous phase. Consequently, pilot studies are necessary to establish the amount of hydrogen peroxide to be used since it is an expensive method of remediation (EPA/600/2-90/006).

Costs for bioremediation is not widely reported. FMC provided cost estimates ranging from \$400,000.00 to \$600,000.00 to clean up a hypothetical spill of 10,000 gallons of jet fuel in a fine gravel formation. Olsen et al

(1986), report that bioreclamation costs are in the range of \$50.00 to \$100.00/ton (\$66.00 to  $$123.00/yd^{-3}$ )(EPA/530/UST-88/001).

## Treatment of Contaminated Groundwater

This section addresses the treatment of gasoline contaminated groundwater from leaking USTs. The most effective processes in groundwater treatment are air stripping, carbon adsorption, biological degradation and treatment trains. Bioremediation is the only treatment that can be utilized in both insitu and non-insitu processes. All these procedures are conducted in conjunction with well systems or more commonly known as pump and treat technologies.

## Air Stripping

According to Canter and Knox (1985), air stripping is a mass transfer process in which a substance in solution in water is transferred to solution in a gas. The rate of mass transfer depends upon several factors according to the following equation.

$$M = K_{L}a (C_{L} - C_{\sigma})$$

where

M = mass of substance transferred per unit time
 and volume (g/hr/m<sup>3</sup>),

 $K_{L}$  = coefficient of mass transfer (m/hr),

a = effective area  $(m^2/m^3)$ , and

 $(C_1 - C_q)$  = driving force (concentration difference

between liquid phase and gas phase  $g/m^3$ ).

Air stripping is used on volatile organics with a high Henry's Law constant. Factors influencing this process are the packing media, tower height and width, flow rate, temperature and the physical and chemical characteristics of the contaminant. The contaminant enters the air stripper from the top, where it is forced through a nozzle that breaks the fluid into small streams or mists. This spreads out the liquid to increase the air/water ratio. As the fluid filters down the media in the tower, its surface area is increased. During this time, a countercurrent of air is forced up and out a vent at the top along with volatiles. Depending on the concentrations being vented, the volatiles may be released or treated before release by filtration or burning. Water collected at the bottom of the tower is sent out as effluent.

Air stripping is well developed and removes organic compounds economically with Henry's constants as low as 10 atm; however, this method is most economical at constants above 50 atm. (Bouwer et al, Aug. 1988). There is a wide variety of devices that may be employed to accomplish gas transfer in water treatment include diffused aeration, the coke tray aerator, the countercurrent packed tower, and the cross-flow tower (Kavanaugh and Trussell, 1980).

Costs in air stripping are variable due to site specific issues, however, Edward Bower, et al (1988), state costs typically range between \$0.15 and \$0.50 per 1000 gallons treated.

#### Carbon Adsorption

Carbon adsorption is a commonly used process to remove volatile organic compounds (VOCs) from contaminated groundwater. Adsorption occurs when an organic molecule is brought to the activated carbon surface and held there by physical and/or chemical forces (Canter and Knox, 1985). Activated carbon has a greater capacity for the adsorption of organic molecules. It is produced by exposing selected carbonaceous materials to a series of treatment procedures referred to as dehydration, carbonization and activation (Benefield et al, 1982).

Adsorption depends on the strength of the molecular attraction between adsorbent and adsorbate, molecular weight, type and characteristic of adsorbent, electrokinetic charge, pH and surface area (PEI Assoc. Inc., 1988). The effectiveness of carbon as a treatment process is due to its

ability to function as an adsorbent for molecules dissolved in water and the large internal surface area. The average surface area of commercially available activated carbon is about 1000  $m^2/g$  (EPA 600/2-90/027).

In selecting carbon adsorption as a remedial process, a strong indicator is the n-octonol:water partition coefficient, which characterizes the hydrophobic nature of the compound (Bouwer et al, Aug. 1988).

The advantage of Granular Activated Carbon (GAC) is the range of both volatile and semi-volatile compounds it effectively treats. GAC can also be sent back for reactivation or recycling.

The cost of activated carbon units depend on the size of the contact unit, which is influenced by the concentrations of the target and nontarget organic compounds in the groundwater, as well as the cleanup goal levels (PEI Assoc. Inc., 1988).

# **Biological Treatment**

The purpose behind biological treatment is to remove organic matter from the groundwater through microbial degradation. This section addresses the treatment of groundwater through well systems or in situ. The process is similar to the processes discussed in Chapter 4, Microbial Degradation. As previously mentioned, microorganisms acclimate readily to hydrocarbons through metabolic processes and converts them to microbial biomass and carbon dioxide.

Heterotrophic microorganisms, or heterotrophs, use the gasoline components as sources of carbon and energy. Three general methods exist by which heterotrophic microorganisms obtain energy; 1) fermentation, 2) aerobic respiration, and 3) anaerobic respiration (Canter and Knox, 1985). The most prevalent form of biological treatment is aerobic and there are several existing biological treatment processes applicable. Modifications of the conventional activated sludge process include the use of pore oxygen-activated sludge, extended aeration and contact stabilization. Fixed film systems include rotating biological discs and trickling filters (PEI Assoc. Inc., 1988).

The biological treatment processes or the surface consists of a large basin into which the contaminated water is introduced, and air or oxygen is introduced by either diffused aeration or mechanical aeration devices. Microorganisms are present in the aeration basin as suspended material. Once the microorganisms have removed the organic material they must be separated by gravity settling. After separation, the biomass increase resulting from synthesis is wasted and the remainder returned to the aeration tank (Canter and Knox, 1985). In fixed film biological processes, the microbes are attached to a medium and the contaminated groundwater is trickled or sprayed on them.

In situ bioremediation operates under the same processes as previously discussed. However, biological treatment is performed in conjunction with pump systems and treat systems where the microorganisms present in the soil or non-indigenous microbes degrade the hydrocarbons. Although they are not clearly defined, several environmental factors are known to influence the capacity of microbial degradation. These factors include dissolved oxygen, pH, temperature, oxidation-reduction potential, availability of mineral nutrients, salinity, soil moisture, the concentration of specific pollutants, and the nutritional quality of dissolved organic carbon in the groundwater (Wilson et al, Winter 1989).

Aerobic and anaerobic conditions studied include enhancement of bioremediation utilizing hydrogen peroxide (Huling, et al, 1990) and nitrate addition (Hutchins, 1991).

Bioremediation is a new technology and a promising approach to many organic contaminants. However, due to the complexity of the subsurface of most UST sites, its applicability, effectiveness and cost is questionable. Before its use, a pilot study should be conducted to justify the cost.

## Treatment Trains

Due to the complexity of the chemical composition of most groundwater and the levels of contamination, no one process is capable of removing all of the contaminants present. After a detailed site characterization and understanding of the site hydrology, a treatment train of processes can be generated.

If there is floating product from the leaking UST, then a skimmer system, one-pump system or two-pump system should be used. If no LNAPL is present, only the dissolved phase in groundwater needs to be addressed. Next an in situ or non in situ approach should be decided. Many factors such as permanent barriers (like buildings, utilities, etc..) regulatory cleanup goals and cost are considered. Groundwater pumped to the surface where it is treated through an air stripper and followed by carbon adsorption works best for gasoline contamination. Depending on the size of the plume and the amount of groundwater to be treated, bioremediation can be utilized. A properly designed treatment train provides the most effective way to treat contaminated groundwater.

#### CHAPTER V

## RISK ASSESSMENT

# Introduction

A risk assessment is a necessary phase in the process of conducting a risk analysis. As explained in the literature review, a risk assessment is conducted at hazardous waste sites (benzene, a component of gasoline, is a known carcinogen and a listed hazardous waste). The Comprehensive Environmental Response, Compensation and Liability Act of 1980, as amended (CERCLA or "Superfund"), establishes a national program for responding to releases of hazardous substances into the environment. The regulation implementing CERCLA is the National Oil and Hazardous Substances Pollution Contingency Plan (NCP). The mandate is to protect human health and the environment from current and potential threats posed by uncontrolled hazardous substance releases from a site in the absence of any actions to control or mitigate these releases (i.e., under an assumption of no action). The risk assessment contributes to the site characterization and subsequent development, evaluation, and selection of a appropriate response alternatives (EPA/540/1-89/002).

Under CERCLA and NCP, remedial actions selected must be cost-effective, and protective of public health. Sites are evaluated through a Remedial Investigation (RI), which defines the nature and extent of contamination, and a Feasibility Study (FS), in which potential remedial alternatives are developed and analyzed. Part of the FS is the risk assessment projecting health impacts resulting from the uncontrolled site.

Risk is defined as the possibility of suffering harm from a hazard. A hazard is a source of risk and refers to a substance or action that can cause harm. A risk assessment refers to the technical assessment of the nature and magnitude of risk.

The Superfund Public Health Evaluation Manual (SPHEM), published in 1986, provides guidance by the U.S. Environmental Protection Agency for conducting a baseline risk assessment. The SPHEM methodology describes the assessment as a multi-step process consisting of the following: (EPA/540/1-86/060)

- Chemicals at the site are identified and indicator chemicals are selected;
- 2. Potential exposure paths are characterized;
- 3. Projected concentrations are compared to standard;
- 4. Human intakes are estimated; and
- 5. Toxicity is evaluated and risks are characterized.

The information obtained from the risk assessment is used to:

- Help determine whether additional response action is necessary at the site;
- 2. Modify preliminary remediation goals;
- 3. Help support selection of the "no action" remedial alternative, where appropriate; and
- 4. Document the magnitude of risk at a site, and the primary causes of that risk. (Cohrssen and Covello, 1989)

All risk assessments are site-specific and vary in the extent of qualitative and quantitative analyses. This depends on the complexity and circumstances of the site, the availability of applicable or relevant and appropriate requirements (ARAR's).

The goal of risk assessment is to estimate the severity and likelihood of harm to human health or the environment occurring from exposure to a substance or activity that under plausible circumstances can cause harm to human health or to the environment.

Analytical procedures used to generate a risk estimate include:

- 1. Source/release assessment
- 2. Exposure assessment
- 3. Dose-response assessment
- 4. Risk characterization

#### Source/Release Assessment

A source/release assessment is applicable to the incidental or accidental release of toxic chemicals or other hazardous materials from a facility or a transportation vessel; storm-water runoff in urban areas; accidental releases of radioactive material from a nuclear power plant; leakage from a lined hazardous-waste landfill, waste pond, or underground storage tank and the incidental or accidental release of pathogenic microorganisms from a research facility or hospital (Cohrssen and Covello, 1989) (See Figure 8).

Four types of quantitative techniques can be used alone or in combination to assess sources and releases: 1. Monitoring,

2. Accident investigation and performance testing,

3. Statistical methods, and

4. Modeling.

Monitoring consists of regular sampling in an area near or around a risk source (such as a leaking underground storage tank) to detect and quantify the amount of harmful gases, vapors, effluents, particles, radioactive particles, organisms and other substances or materials escaping from the source.

Category I-Sources designed to discharge substances Subsurface percolation (e.g., septic tanks and cesspools) Injection wells Hazardous waste Non-hazardous waste (e.g., brine disposal and drainage) Non-waste (e.g., enhanced recovery, artificial recharge, solution mining, and in-situ mining) Land application Wastewater (e.g., spray irrigation) Wastewater byproducts (e.g.,. sludge) Hazardous waste Non-hazardous waste Category II-Sources designed to store, treat, and/or dispose of substances; discharge through unplanned release Landfills Industrial hazardous waste Industrial non-hazardous waste Municipal sanitary Open dumps, including illegal dumping (waste) Residential (or local) disposal (waste) Surface impoundments Hazardous waste Non-hazardous waste Waste tailings Waste piles Hazardous waste Non-hazardous waste Materials stockpiles (non-waste) Graveyards Animal burial Aboveground storage tanks Hazardous waste Non-hazardous waste Non-waste Category VI-Naturally occurring sources whose discharge is created and/or exacerbated by humań activity Groundwater-surface water interactions Natural leaching Salt-water intrusion/brackish water upconing (or intrusion of other poor-quality natural water)

Underground storage tanks Hazardous waste Non-hazardous waste Non-waste Containers Hazardous waste Non-hazardous waste Non-waste Open burning and detonation sites Radioactive disposal sites Category III-Sources designed to retain substances during transport or transmission Pipelines Hazardous waste Non-hazardous waste Non-waste Materials transport and transfer operations Hazardous waste Non-hazardous waste Non-waste Category IV-Sources discharging substances as consequence of other planned activities Irrigation practices (e.g., return flow) Pesticide applications Fertilizer applications Animal feeding operations De-icing salts applications Urban runoff Percolation of atmospheric pollutants Mining and mine drainage Surface mine-related Underground mine-related

Category V—Sources providing conduit or inducing discharge through altered flow patterns Production wells Oil (and gas) wells Geothermal and heat recovery wells Water supply wells Other wells (non-waste) Monitoring wells Exploration wells Construction excavation

SOURCE: U.S. Office of Technology Assessment: Protecting the Nation's Ground Water from Contamination (OTA-0-233). Washington, DC, 1984.

Figure 8.

3. Sources of Groundwater Contamination

Accident investigation involves the interpretation of the causes and sequences of events after a disruption in a system. Performance testing assesses a system's behavior under controlled and stressed conditions that may cause a release of toxic substances or materials.

Statistical methods are useful to study the frequency of releases to certain activities. Sometimes the risk analyst must assume that the events are only random events.

Depending on the amount of data available and the type of data the use of models can be characterized by graphic representation such as fault trees or event trees. Fault trees describe in graphic form the specific chain of events or conditions required for a release to occur. Fault trees begin at the undesired event and work backwards. Event trees are similar only they begin with the undesired initiating event and work forward.

#### Exposure Assessment

An exposure assessment is conducted to estimate the magnitude of actual and/or potential exposure to humans, the frequency and duration of these exposures, and the pathways by which humans are potentially exposed. Exposure assessments include (1) risk agents that target organisms, species, or environments, (2) how much exposure, (3) in what way, (4) for how long, and (5) under what circumstances (Cohrssen and Covello, 1989).

For hazardous materials such as gasoline from leaking underground storage tanks, exposure assessments use three kinds of approaches:

1) analogies,

2) monitoring, and

3) modeling.

Environmental transport and fate of a risk agent such as gasoline are more accurately predicted using the actual measurements of soil and groundwater concentrations. If this data is not available then an analogy with similar (physical and chemical) characteristics should be used for fate and transport (EPA/540/1-89/001).

Exposure monitoring provides the most accurate information about exposure. There are two kinds of exposure monitoring, personal and ambient monitoring. Personal monitoring includes sampling of the air inhaled and the water consumed by the person wearing the monitoring device. Ambient monitoring , in contrast to personal monitoring involves collecting samples from the air, water or soil at fixed locations and analyzing the concentrations of hazardous substances at the different locations.

Exposure modeling simulates the behavior of risk agents in the environment and are used when monitoring data are either inadequate or inappropriate. The variety of models include: (Cohrssen and Covello, 1989) (1) atmospheric models,

(2) surface-water models,

(3) groundwater and unsaturated-zone models,

(4) multimedia models,

(5) food chain models, and

(6) modeling the environmental behavior of microorganisms

Dose-Response Assessment

A dose-response assessment is the process of quantitatively evaluating the toxicity information and characterizing the relationship between the dose of the contaminant administered or received and the incidence of adverse health effects in the exposed population. From a dose-response curve, quantitative toxicity values are derived and are used to determine amount of risk for the exposed population occurring at different exposure levels.

Epidemiological and toxicological studies are used in dose-response assessments. Epidemiological studies are concerned with the patterns of disease in human populations under conditions as well controlled as the circumstances permit. Toxicological studies deal broadly with controlled laboratory experimentation, mostly on animals, and invitro. Epidemiology studies have excellent relevancy while the relevancy of toxicological studies are unknown. Toxicological studies provide a toxicity value for a wide range of chemicals. Problems in assessing risk however arises from correlating risk from animals to humans. Differences due to size, weight, and surface area are great. Also animal studies are conducted using large doses on small animals. This makes the extrapolation of the dose-response curve to small doses difficult. At what level of response does a dose become a risk ? Uncertainty is a large factor in the entire risk assessment process.

#### Risk Characterization

The fourth and final step is the risk characterization process. The risk characterization summarizes and combines outputs of the exposure and dose-response assessments to characterize risk in both quantitative and qualitative form.

For a site, it is important to characterize the potential for adverse health effects to occur. This is done by estimating the cancer risks and an estimate of noncarcinogenic compounds. At this point of the risk assessment all uncertainties in each phase, especially the doseresponse assessment, must be evaluated. The final step is to summarize the risk information to the target audience and how to release this information.

# CHAPTER VI

# CASE STUDY

## Introduction

This chapter contains an intensive site characterization and remediation of an industrial site. The different steps of the site characterization will be presented with the corrective action plan, the groundwater remediation system, and a risk assessment of gasoline vapor exposure to contractors and engineers.

## Background Information

Contamination at the project site was discovered during an environmental assessment provided to the lending institution for a real estate transaction. This knowledge of environmental liability benefitted the lender by requiring the seller to share cost in the clean up.

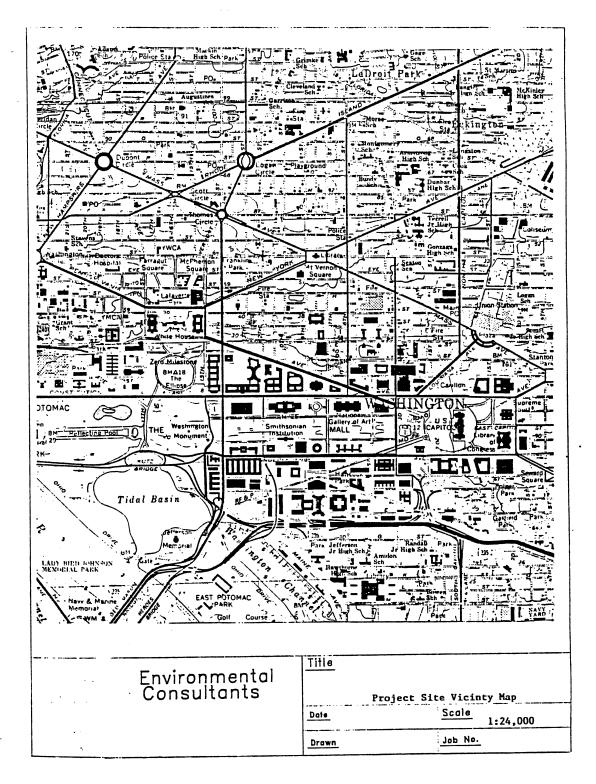
#### Site Characterization

There were several phases of investigation towards an in-depth site characterization, and those studies are reviewed in this chapter.

# Location and General Physiography

The project site is located in an industrial area in Washington, D.C. The proximity of the Tidal Basin, the Potomac River, and other features like the Capital Building, the Washington Monument, etc. can be seen in Figure 9.

The Washington, D. C. area contains two distinctly different physiographic provinces: the Piedmont and the Coastal Plain. The Fall Line (Figure 10) separates the Piedmont on the west from the Coastal Plain on the east (Moore, 1989). Subsurface investigation of the project site proved it to be in the Coastal Plain physiographic province. The Coastal Plain rocks are composed of unconsolidated sand, gravel and clay of Cretaceous, Tertiary and Quaternary Age. Groundwater in the Coastal Plain fills the pore spaces in sand and gravel aquifers. Most of the needs of the Washington Metropolitan area are provided by the Potomac River.



# Figure 9. Project Site Vicinity Map

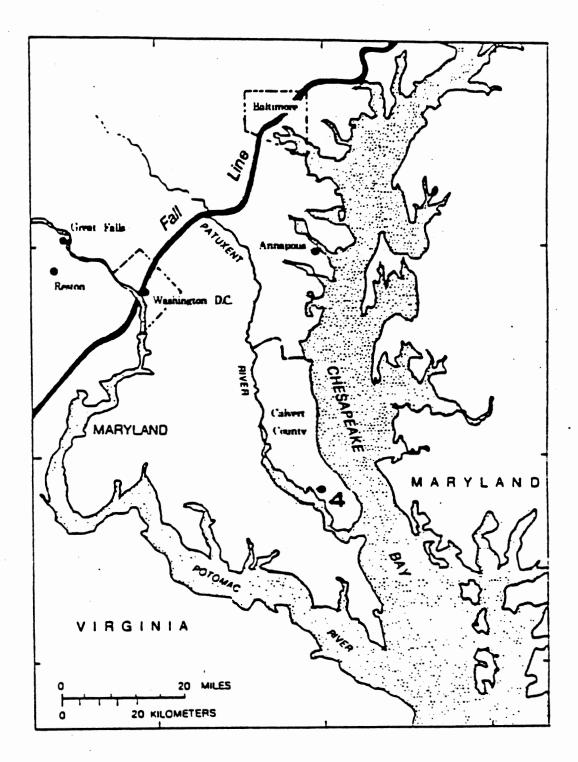


Figure 10. The Fall Line

# Site Description

During preliminary investigations several environmental concerns were found as seen in Figure 11. Large piles of fill, buried refuse, abandoned drums of PCE and many UST's were observed throughout the property. Records from the D. C. Environmental Control, UST Division, revealed several abandoned UST's and releases from the adjacent property to the north. To the west a warehouse was suspected of having underground storage tanks, but no records could be found to prove their existence. The Metro Railway system bounded the property to the east with no observable environmental concerns. The Metro Station was located to the south of the investigated site and posed no apparent environmental hazard. The buildings on the project site consisted of a main office building, a four-story warehouse with a loading dock and asphalt parking lots on the remaining property (Please refer to Figure 11). Surface gradient in the area is from north to south, towards the Potomac River.

# <u>Soil</u>

The project site lies in the Coastal Plains physiographic province. The soils composed of transported deposits of sand, silt and clay of the Wicomico Formation. The upper 10 to 12 feet of soil consists of brown/orange, moist, medium stiff, silty clay and clayey silts. Underlying this soil type is a gray, saturated, loose, silty

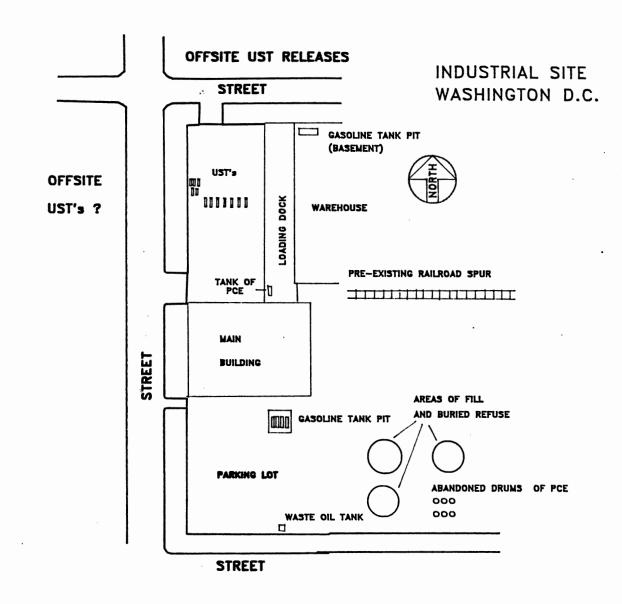


Figure 11. Project Site Map

sand, which compromises the upper unconfined aquifer media on site. Figure 12 is a log of a soil boring used to record the soil types found, their depth, soil descriptions, depth to water, method of sampling and other information necessary to delineate soil contamination.

A soil sampling and analysis program was conducted in the NW corner of the investigated site. Initially, each soil boring was drilled through concrete with a decontaminated hollow stem auger. Next, a decontaminated 18 inch split spoon was hammered into the soil and a soil sample was recovered. After logging of the soil sample, the soil was placed in a glass jar with a teflon lid and labeled accordingly. After split spoon sampling, the sampled interval was drilled with a hollow stem auger to the next sampling depth. This cycle of split spoon sampling followed by drilling continued until the total depth of the soil boring was reached.

Careful observation of Figure 12 shows at 19 feet below surface grade a dark, moist, soft, highly organic clay with plant roots and rotting wood. This organic clay pinches out towards the west. Below this organic clay, the soil grades back into the same silty sand found above the clay.

During the soil sampling process, a cooler with ice was used to preserve the samples until delivery to an accredited laboratory for TPH and BTEX analyses.

	F SOIL BORING	DRILLER		PR	OJECT			BC	DRING	SB - 1
200 01		DRILL METHOD		CLI	ENT				AGE	OF
	Environmental Consultants	1			CATION		-	01	B No.	
		BOREHOLE DIAMET		PAT	E START			LO	GGED	 Βγ
		OTHER	N/A		E END			СН	ECKED	BMGN Ny
PETHPID	SOIL DESCRI		SOIL	DEPTH (FEET)	BLOWS/8"		INCHES	INCHES	TYPE	ADDNL. INFO
				-						
				<b>[</b> 1						
2	Brown/orange, moist,	medium		2						
	stiff, silty clay			X 3	4,4,4	1	18	10	SS	
- 3			~	Ē						
- 4	Gray/orange, moist, a silty clay	stiff,	CL	- 4						
_ 5				¥ 5	4,7,5	2	18	11	SS	
<b>6</b>				_ 6						
7	Gray/orange, moist,	very stiff,		_ 7		_	18	16	SS	
	silty clay			8	4,7,9	3	10	10	22	
	Same as above with 1	ast 5" grad-		- 9						
	ing into lt. brown, a loose, silty sand N			-	6,6,4		18	16	SS	
		-		F	0,0,4		10			
<b>2</b>			21	- 2						
3				Γ 3						
				<b>⊨</b> 4						
<b>5</b>	Gray, saturated, loo silty sand	8 <b>e</b> ,		LIB	6,6,2	5	18	14	SS	
				+ 6						
- "				F,						
- 7				<b>⊦</b> 7					1	
8	Same as shows anoth	ng into		F 8						
- 9	Same as above, gradi dark, moist, soft, h nic clay w/ plant ro	ighly orga-		9						
_ o	rotting wood		OL	<b>x</b> 20	3,3,3	6	18	16	SS	
	Same as above, gradi	ing into	-51-			,	10	10	SS	
	gray, saturated, loc	ose silty sa	nd @25	X	4,2,8	7	18	1.10	1 33	<b>I</b> .

Figure 12. Log of Soil Boring

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A Chain of Custody (COC) record was provided for all samples obtained for analysis. Figure 13 is a copy of a Chain of Custody record used at the investigated site. The purpose of the Chain of Custody record is to provide written documentation that all samples developed are properly handled within Quality Assurance and Quality Control (QA/QC) procedures. In this record, all persons in possession of the samples listed on the record sign for receipt and release of the samples, thus providing sample integrity.

The analytical results for TPH and BTEX analyses normally takes two weeks turn around time unless a rush is requested and a premium paid for the service. Figure 14 shows an example of analytical results for TPH analysis. Note the detection limit for this analysis and laboratory method is in parts per million (ppm). Analytical results for BTEX, EPA Method 602, is found in Figure 15, with a detection limit in parts per billion (ppb).

Once analytical results are available, determination of the extent of contamination is possible. Figure 16 shows the locations of the soil borings and monitoring wells onsite. Using the analytical results and the locations, a soil contamination contour map was developed. The highest concentrations of hydrocarbon contamination was determined to be at the static water level, where in some borings, free product was present. A soil isopleth map, at 10 foot depth below surface grade was developed. The highest levels of

-הסמדיניבי • Client/Job No: \_\_\_\_ Job Name: \_\_

CHAIN OF CUSTODY RECORD								
Sample No.	Lab I.D. No.	Date	Time	Matrix	No. of Containers	Analysis Requested/Remarks		
5B-7B		8-3/-89		5016	1	TPH, BTX		
5B-8A		8-31-89	-	SOIL	1	TPH, BTX		
53-8B		8-31-89		SOIL	1	TPH, BTX		
5B-9A		9-1-89		SOIL	1	TPH, BTX		
53-93		9-1-89		Sorl	1	TPH, BTX		
•								
						<u> </u>		
Comments: I lease turnaround results by the Friday per our plane conversation								
Relinquished by: Bluit Ward Date: 9-5-89 Shipment Method:								
Received by:         State:         9-5-89         Relinquished by:         Date:            Time:         1800         HRS         Time:								
Received by: كالمحمد عليه المعالي Date: 9-6-59 Relinquished by: Date: Time: 8: 25								
Final Disposition of Samples:								
; Date: Time:								

Pink. Field Copy - Yellow. Lab Copy - White-Original - To be returned with results.

Figure 13. Chain of Custody Record

# MARTEL

MARTEL LABORATORY SERVICES, INC.	1025 Cromwell Bridge Road Baltimore, Mary 5920 North Belt, Suite 111 Houston, Texas Capital Airport Springfield, Illinois 62707 (2	7396 (713) 441	
Client Identification: Log Identification: W-4819			
Page 2			
Sample Id: SB-5A			
Petroleum Hydrocarbons Volatile Organic Compounds	SM 503 E EPA 602	22 588	ppm attached
Sample Id: SB-5B			
Petroleum Hydrocarbons Volatile Organic Compounds	SM 503 E EPA 602	210 see	ppm attached
Sample Id: SB-5C	· ·		
Petroleum Hydrocarbons Volatile Organic Compounds	SM 503 E EPA 602	23 500	ppm attached
Sample Id: SB-6A			
Petroleum Hydrocarbons Volatile Organic Compounds	SM 503 E EPA 602	<20 500	ppm attached
Sample Id: SB-6B			
Petroleum Hydrocarbons Volatile Organic Compounds	SM 503 E EPA 602	<20 500	ppm attached
Sample Id: SB-7A	-		
Petroleum Hydrocarbons Volatile Organic Compounds	SM 503 E EPA 602	<20 500	ppm attached

FACS 301-821-1054

A GECHEX Company

Figure 14. TPH Analytical Results

# MARTEL

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#### MARTELSBORATORY SERVICES.INC. 1025 Cromwell Bridge Road Baltimore. Maryland 21204 (301) 825-7790 5920 North Belt. Suite 111 Houston. Texas 77396 (713) 441-4965 EPA Fridrary Porraitantino friary for 122-0009 Volatile Organic Analysis, Method 602

Analytical Parameter	Result	Detection Limit	Units
** SB-5B			
Benzene	57000	<50	ug/kg
Toluene	230000	<50	ug/kg
Ethylbenzene	230000	< 50	ug/kg
m-Xylene	360000	<50	ug/kg
(o- + p-) Xylenes	190000	<50	ug/kg

FACS 301 921-1054

Figure 15. BTEX Analytical Results

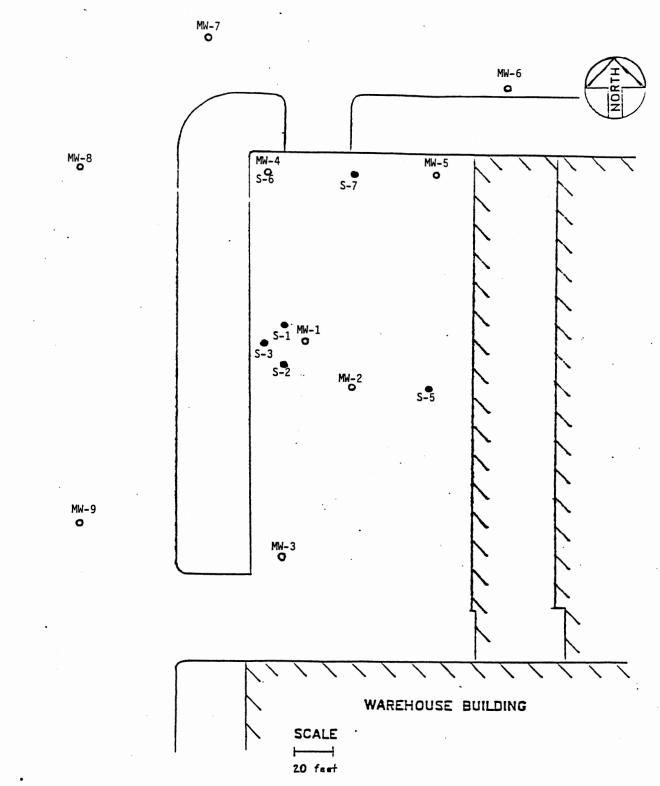


Figure 16. Soil Boring and Monitoring Well Location Map

contamination were found in soil borings S-1, S-2, S-3 and Monitoring Well-1, near a previously existing dispenser with three (3) 10,000 gallon UST's. The soil isopleth map (see figure 17) showed levels of TPH high enough to notice the effect of hydrocarbon migration from the adjacent property to the north where UST's releases had been reported. The majority of the northwest corner showed soil contamination exceeding 100 ppm. The shape of the plume gave early indication of groundwater flow to the southsouthwest towards the Tidal Basin and the Potomac River.

#### Groundwater

Once significant soil contamination had been observed, it was necessary to address the possibility of groundwater contamination. Several monitoring wells were placed in the northwest corner as well as some wells in the street, adjacent to properties with known or suspected hydrocarbon contamination.

During the installation of monitoring wells, proper design and construction is extremely important. Figure 18 is a diagram of a standard overburden groundwater monitoring well. The installation of a groundwater monitoring well was conducted with the same hollow-stem auger rotary rig used for the soil borings. Decontaminated hollow stem augers drilled a borehole with enough diameter for a four inch PVC cased well. Once the borehole is drilled, depth to water is

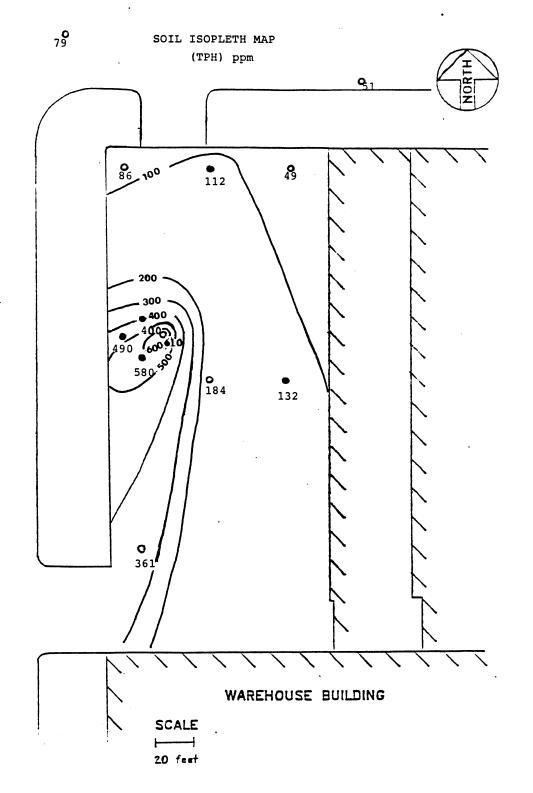


Figure 17. Soil Isopleth Map

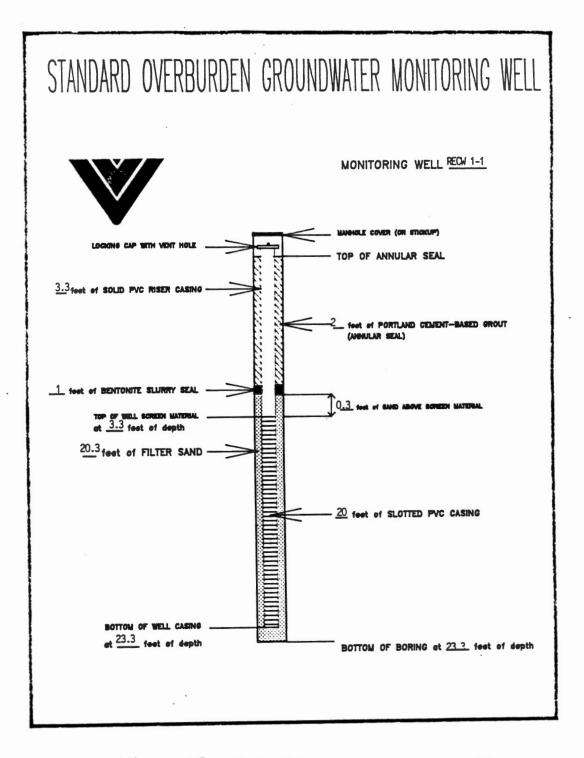


Figure 18. Groundwater Monitoring Well

determined for a proper screening interval. Since most petroleum contamination is located in the uppermost aquifer with some floating product, it is important to screen high enough to detect the floating product. The annular space must be at least 2 inches for good well development. Coarse sand was used to fill the annular space up to 2 feet above the top of the well screen. A minimum of 2 feet of bentonite was used to seal the well from contamination or infiltration from above. The remaining annular space was filled with a portland cement-based grout all the way to surface. A locking cap was in place to protect the groundwater from infiltration or intentional contamination. A flush mount cover was then placed above the well.

Groundwater samples were obtained from all monitoring wells for laboratory analyses. Proper procedure for obtaining groundwater samples requires the well to be developed or purged of 3 x (times) the volume of water in each well. To avoid cross-contamination between wells, each well was designated a specific bailer. All bailers were packaged decontaminated and were disposable after use. It is important that samples obtained for gas chromatography (GC) analysis be free of headspace in the vial. The borosilicate vials used were pre-cleaned and certified to exact EPA specifications. The preservation method of the groundwater samples was a cooler, just like the soil samples.

A Chain of Custody record was provided for all samples to insure sample integrity.

All monitoring wells were surveyed for exact location and for elevation within .01 of an inch. Depth to water measurements were taken in all wells, on the same day to avoid fluctuations in the static level. With the elevation of the wells and the depth to water measurements, an elevation for groundwater in mean sea level (MSL) was determined. A groundwater contour map was developed from this information and the direction of groundwater flow established. In Figure 19, the groundwater flow direction was to the south-southwest as predicted by the soil isopleth map (Figure 17, pg. 85) and the local topography.

Figure 20 is a groundwater contamination contour map. The data used for this map is the TPH analytical results in parts per million (ppm). The clean up goal was set at 100 ppm (TPH). The direction of migration of the contaminant plume concurs with the direction of groundwater flow (fig. 19). The groundwater plume map revealed product not only migrating off-site but also revealed free product migration from the adjacent property to the north. The knowledge of a source for groundwater contamination upgradient from the investigated site, complicated the choice of groundwater treatment.

Free product was encountered in monitoring wells MW-1 and MW-7. The groundwater contamination contour map (fig.

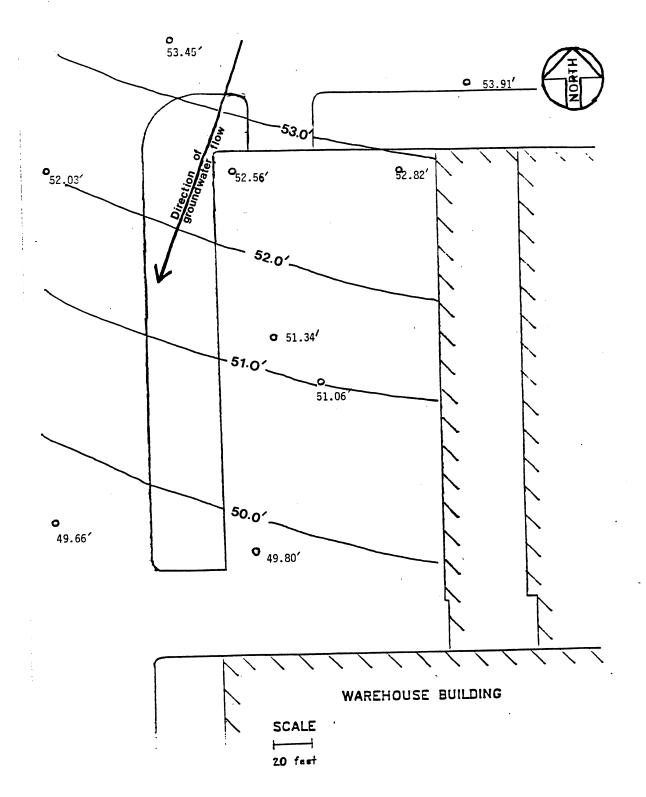


Figure 19. Groundwater Contour Map

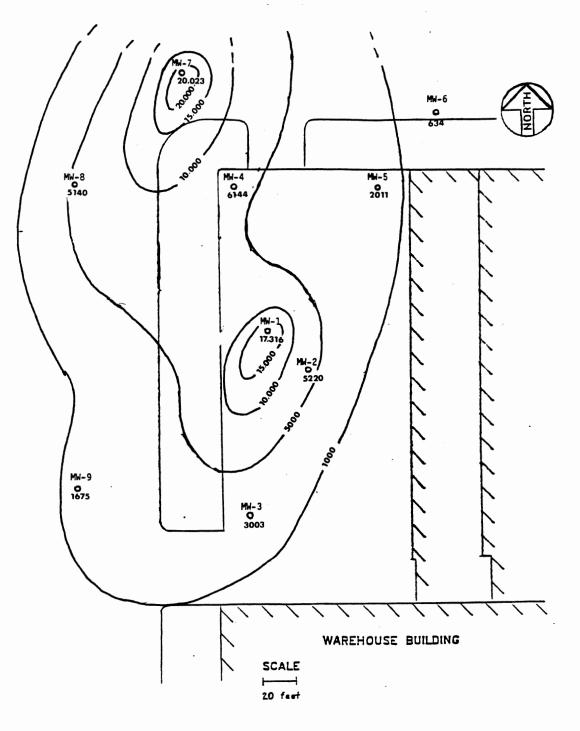


Figure 20. Groundwater Contamination Contour Map (TPH) ppm

20) shows the effect of free product and its migration. D.C. Environmental Control Division was notified of the free product encountered but immediate action was not requested. The presence of free product in MW-7 provided D.C. Environmental with the authority to demand a site characterization from the adjacent property owners.

# Remediation

For a proper corrective action plan to remediate the site, additional studies were performed. All options for remediation were first reviewed through and accepted by D. C. Environmental Control Division and the client prior to the initiation of each.

#### Bioremediation Feasibility Study

Due to the amount of contaminated soil, the first options revolved around in-situ treatments. One option that was explored was bioremediation. Soil samples from two (2) locations and groundwater samples were sent to a bioremediation firm for the feasibility study.

The feasibility study was conducted to assess the biotreatability of soils and groundwater from the site. Groundwater (GW) samples, highly contaminated soil from the tank pit (subsequently referred to as "pit soil") and less contaminated soil from a boring about 35 feet from the tank pit (subsequently referred to as "peripheral soil") were tested. The purpose of testing was:

- To evaluate possible toxicity or inhibition of soil and/or groundwater contaminants to microbial growth.
- To verify that microbes can substantially reduce contaminant levels when supplemented with appropriate nutrients.

Testing was conducted by monitoring microbial oxygen uptake during treatment and by petroleum hydrocarbon analysis of aqueous and soil fractions before and after biological treatment under batch process conditions. This type of screening study was used to determine the suitability of surface reactor treatment of groundwater and/or insitu treatment of soil and groundwater by nutrient augmentation. Samples of ground water and each of the two soil samples were analyzed for total petroleum hydrocarbons (TPH) by freon extraction and infrared spectroscopic determination (Standard Methods for the Examination of Water and Wastewater, 16th ed., APHA, 1985; Methods 503 B, C, E.).

In these experiments, an increase in concentration of the contaminated sample, either groundwater or soil, will increase oxygen uptake if the sample contains biodegradable organic compounds which are not toxic or inhibitory to microbial growth; however, oxygen uptake decreases will occur if the test sample contains inhibitory or toxic constituents.

The conclusions and recommendations of the bioremediation feasibility study are as follows:

- Soil samples were not mixed to homogeneity due to limitations imposed to prevent volatile contaminant loss. Heterogeneity of soil samples prevented confirmation of TPH degradation by analysis of treated soil residues.
- 2. Both GW and Pit Soils showed evidence of microbial toxicity. Respirometry data indicated a lack of response by the microbial population as substrate concentration (Figures 21 & 22).
- 3. Both soil samples showed indications of TPH biodegradation of acceptable rates. Although not confirmed by TPH analyses, the oxygen uptake for Peripheral Soil (Figure 23, 50 g Soil) and Pit Soil (Figure 22) all agreed fairly closely with a TPH degradation rate of 600 to 850 mg TPH/kg per 160 hours. This rate is equivalent to 100 mg TPH/kg per 160 hours.

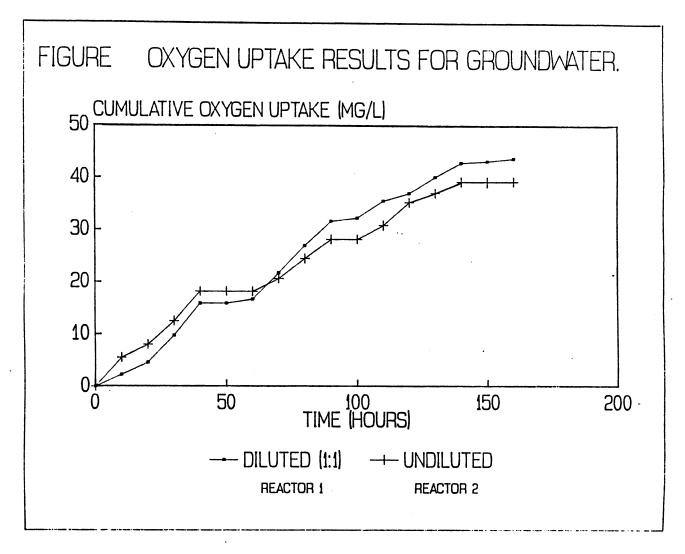


Figure 21. Oxygen Uptake Results for Groundwater

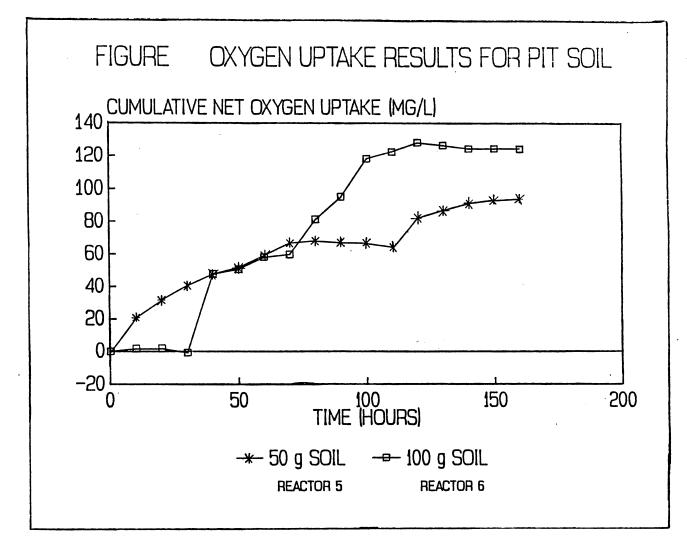


Figure 22. Oxygen Uptake Results for Pit Soil

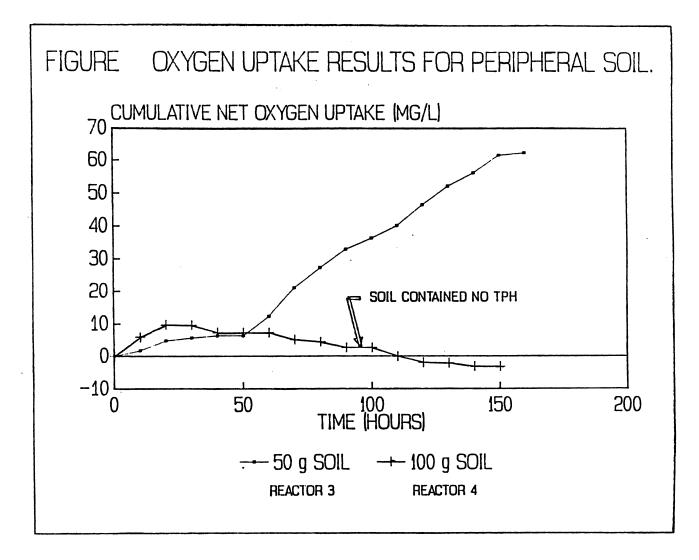


Figure 23. Oxygen Uptake Results for Peripheral Soil

- 4. The data obtained is not conclusive. Ambiguous results for toxicity (Peripheral Soil, Figure 23) and the lack of confirmation of TPH removal suggest further testing will be required.
- 5. No recommendation to proceed with bioremediation can be made without additional testing. The indications of toxicity noted above are sufficient to require a cautious approach. Further testing to clarify the severity of inhibition under process conditions must precede any decision to pursue bioremediation.

A representative from the bioremediation firm met with personnel to review and discuss the methodology and results of the feasibility study for the site. Due to the nonhomogeneity and low permeability of the soils, it was determined that efficient and effective remediation of the site utilizing in-situ biological techniques was not Information from the pumping test was used for possible. percolation rates of the soil. Since the soils on site have a very low permeability, groundwater cannot be effectively filtered. If water containing nutrients and oxygen are not able to percolate through all soil zones, the naturally occurring micro-organisms on site cannot thrive in the low permeability zones and thus cannot biodegrade the contaminants. The representative from the bioremediation

..... 98

firm stated that due to encountered conditions, 100 per cent restoration was not possible and a time frame for any significant percentage of cleanup could not be given.

#### Corrective Action Plan

Data obtained through the soil/groundwater sampling and analysis program in conjunction with the bioremediation feasibility study indicated in-situ treatment of the contaminated soil was not feasible. After careful studies for soil disposal, it was determined that soil excavation and landfill disposal was the best option. During excavation, any underground storage tanks would be removed and the excavation backfilled with crush and run CR-6 gravel. Groundwater contamination remediation would require a slurry wall to the north to impede hydrocarbon contamination migrating on-site. A groundwater pumping test would be performed to determine aquifer characteristics necessary for the groundwater remediation equipment and to determine the location and number of recovery wells.

## Slurry Wall

As previously stated, a slurry wall was constructed on the northern and western property boundaries, as evidenced in Figure 24 (pg. 102). A two (2) foot wide by twenty-five (25) foot deep trench was dug and filled with a 50/50 bentonite/cement slurry. At the northwest corner, metal sheeting was installed to reinforce the slurry wall. During this process, previous foundations and fill were encountered slowly down the construction. It was estimated it may take many years for the slurry to set, and maybe never for the section of the wall underwater.

## Soil Excavation

Approximately 67,000 tons of contaminated soil were excavated and transported to a landfill in Virginia. Weeks in advance, several analyses were performed on the contaminated soil before written authorization was received from the landfill disposal facility.

Two large backhoes worked 14 hours a day excavating and loading trucks with 10 to 12 tons of soil at a time. Soils being excavated were constantly monitored to insure that only highly-contaminated soils left the site. Manifests of transport and eventually manifests of disposal were received for documentation. This process of screening, excavating and transporting endured for 8 days. At one point 52 trucks were available, transporting the soil to Virginia. Strict DOT regulations were adhered to by the transportation company.

During the excavation, several unknown underground storage tanks were discovered. Permits and all regulations pertaining to UST closures were followed with strict adherence. A total of fourteen (14) UST's were removed, with eleven (11) of the UST's having been abandoned in place by slurry fill method. The Fire Marshall representative present during removal noted contamination extruding from the slurry filled UST's. Only the upper portion of the slurry fill had set and the rest contained sand, water and residual hydrocarbons. The slurry fill from the UST's was placed with the excavated soils to be landfilled. The metal from the UST's was steam-cleaned and cut in pieces before being sent to a scrap yard.

Appropriate backfill material, crush and run CR-6 gravel, was used and the process only lasted 3 days. The source was relatively close and more economic than the excavation process.

## Characterization of Site Hydrogeology

Several recovery wells for the groundwater remediation system were installed and their locations can be observed in Figure 24. A hydrogeologic investigatory program was conducted to determine the most effective plan of remediation.

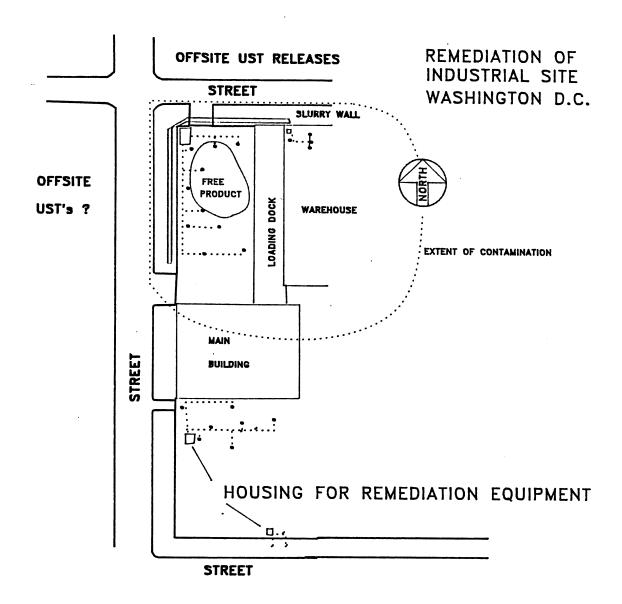


Figure 24. Remediation Site Map

In preparation for the pumping test, a monitoring well was selected for proper well development. The development of the pumping well is of utmost importance. Development reduces the amount of clay and silt in and near the borehole of the well, which if left could inhibit optimum hydraulic performance and yield incorrect data for the calculation of aquifer characteristics. Prior to this development, a permit was obtained from Mr. Tony Butani from the District of Columbia Division of Public Waterworks, Pretreatment Division.

In November, 1989, geologists used a 1/2 horsepower submersible pump to develop monitoring well MW-1. Monitoring well MW-1 was selected as the pumping well due to its greater available drawdown for pumping than any of the other site wells. After several hours of surging and pumping of monitoring well MW-1, the discharge from the well was clean enough to conduct a pumping test.

Equipment for conducting the pumping test was assembled on site. Equipment included a granular activated carbon (GAC) canister, an apparatus designed to adjust the pumping rate, a flow meter, and a Hermit Data Logger with pressure transducers to monitor the water level in all wells.

Before conducting the pumping test, a step-drawdown test was conducted to determine the optimum pumping rate for the aquifer test. The step drawdown test is a series of increasing pumping rates applied to the pumping well over equal time intervals per pumping rate. The drawdown vs. time is observed during each pumping rate and plotted on a semi-logarithmic paper. A line is drawn through the data points and extrapolated until the line intersects the desired length of time for the test. At high pumping rates, the pumping well will be dewatered before 24 hours. By the same token, low pumping rates will not cause sufficient drawdown in the pumping well to stress the aquifer, and thus will not allow the accurate determination of aquifer parameters. After conducting the step drawdown test, the pumping rate selected was 1.50 gallons per minute (gpm). This was an early indication of the aquifer's low permeability. The pumping well was allowed to return to static water level.

Record keeping of the water levels in the pumping well and the observation well at various times was critical. Manual water level measurements for the pumped well were recorded at the times in Table I.

## TABLE I

## RECORD KEEPING OF WATER LEVEL MEASUREMENTS FOR PUMPING WELL

Time Since Pumping Started inutes)	Measurement Interval (minutes)
0- 10	2
10-30	5
30-45	15
45-1440	30

Water level measurements in the observation wells were recorded at the times in Table II.

## TABLE II

RECORD KEEPING OF WATER LEVEL MEASUREMENTS FOR OBSERVATION WELLS

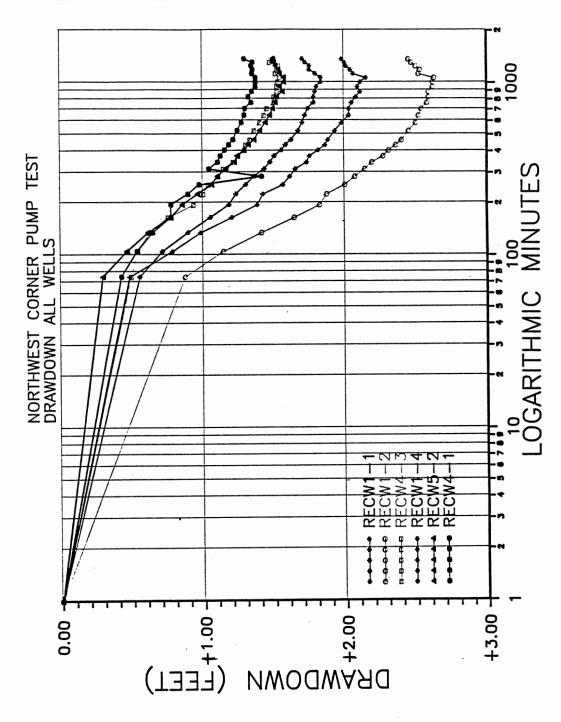
Time	Since Pumping (minutes)	Started	Measurement (minu	
	0-30			10
	30-1440			30

A record of time and drawdown data in the pumping well and observation wells were used to calculate the aquifer characteristics. The data obtained from the pumping test was plotted on semi-logarithmic graph paper with drawdown on the y-axis and time, in minutes, on the logarithmic x-axis. A straight line that best fits the data was drawn through the points.

A time vs. drawdown graph of the observation well was produced from the pumping test data and a straight line was drawn through the points. Please refer to Figure 25.

From the time vs. drawdown graphs important aquifer characteristics can be calculated. Using the time vs. drawdown graph for the observation well, the transmissivity (T), hydraulic conductivity (K), and storativity (S) for the aquifer were determined. The coefficient of transmissivity (T) of an aquifer is the rate at which water flows through a unit width vertical strip of the aquifer extending through the full saturated thickness, under a hydraulic gradient of 1 (100 per cent). Transmissivity is an indication of how much water will move through the formation. The coefficient of storage, S, of an aquifer represents the volume of water released from storage per unit of aquifer storage area per unit change in head. This is an indication of how much water can be removed by pumping or draining.

The coefficient of transmissivity is calculated from the pumping rate and slope of the time - drawdown graph by using the modified Jacob equation: (Driscoll, 1987)



# Figure 25.

Time - Drawdown Graph

$$T = \frac{2640}{\Delta s}$$

where

T = coefficient of transmissivity, in gpd/ft Q = pumping rate, in gallons per minute, gpm  $\Delta s$  = (read "delta s") slope of the time drawdown graph expressed as the change in drawdown between any two times on the log scale whose ratio is 10 (one log cycle).

From the time - drawdown graph of the observation well,  $\Delta$ s is 1.3 feet, and Q equals 1.5 gpm, So:

The coefficient of storage is also readily calculated from the time-drawdown graph by using the zero - drawdown intercept of the straight line as one of the terms in the equation.

$$S = \frac{0.3T t_{\circ}}{r^2}$$

where

r = distance, in feet, from the pumped well to the observation well where the drawdown measurements were made.

From the time - drawdown graph,  $t_o = 54$  minutes or 0.0375 day,

T = 305 gpd/ft and r = 37 feet.

Therefore:

$$S = \frac{0.3 \times 305 \times 0.0375}{(37)^2} = 2.5 \times 10^{-3}$$

The hydraulic conductivity, K, is the rate of flow of water in gallons per day through a cross section of one square foot under a unit hydraulic gradient (Fetter, 1988).

$$K = T/b$$

where

T = coefficient of transmissivity, in gpd/ft b - saturated aquifer thickness, in ft. T = 30 gpd/ft, b = 15 ft. K =  $\frac{305}{15}$  = 20.3 gpd/ft

Using the calculations from the time -drawdown graphs, it is possible to construct a semilog distance - drawdown graph. The distance - drawdown graph helps define the cone of depression created by the pumping well. With the distance-drawdown graph, see Figure 26, the amount of

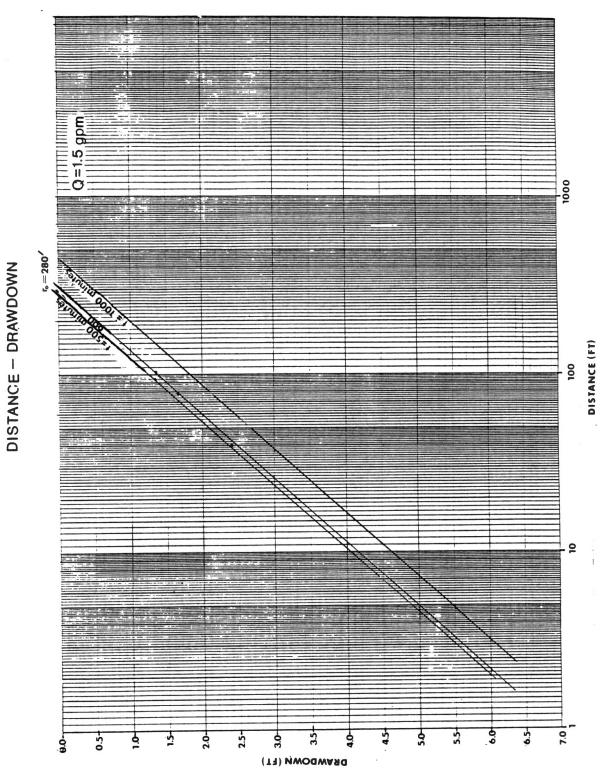


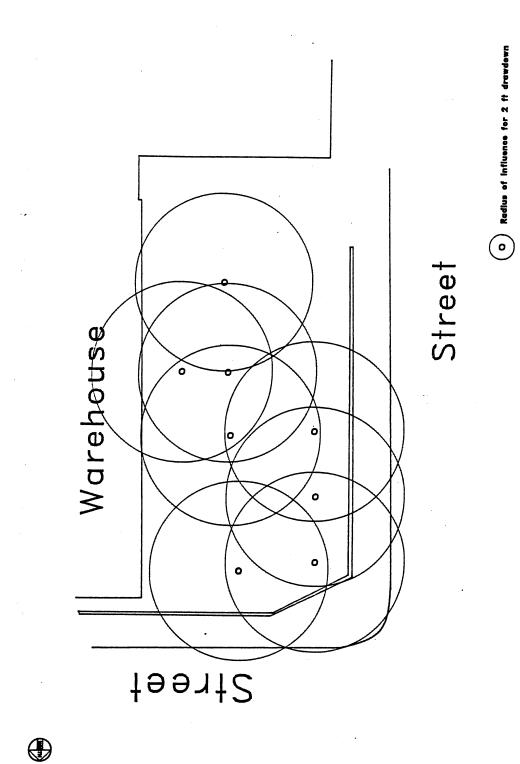
Figure 26. Distance - Drawdown Graph

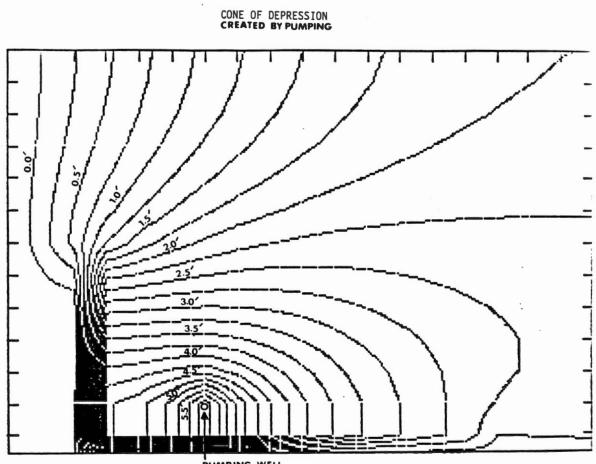
drawdown in the water table can be determined at any distance from the pumped well. Once the required amount of drawdown is determined, a radius of influence can be found for the pumping of a recovery well. To construct the distance - drawdown graph, a drawdown is selected at a certain time from the time - drawdown graph. With the known radius of the observation well from the pumping well, a data point can be plotted.

The value of As for the distance - drawdown graph is twice the As for the time drawdown graph. For a given aquifer and a given pumping rate, this ratio for the slopes of the two straight lines is a fixed relationship. Therefore, when s is determined from the time - drawdown graph, the slope of the curve on the distance - drawdown graph should be twice as great if the well is pumped at the same rate. Refer to Figure 26 for the distance - drawdown graph (pg. 110).

The radius of influence was determined and that radius plotted for all recovery wells, as revealed in Figure 27. From this diagram several combinations of recovery wells can be used for groundwater remediation.

Presence of the slurry wall and its effectiveness was examined by plotting the water elevations during the pumping test. The cone of depression creating by the test revealed the negative boundary effect of the slurry wall. Figure 28 reflects this conclusion.





PUMPING WELL

Figure 28. Cone of Depression

#### Groundwater Remediation System

Based upon an analysis of all site data obtained, a groundwater remediation system design was developed, Figure 29 shows a flow diagram of the system.

Submersible pumps (1/2 hp) were placed one (1) foot above the total depth of each recovery well. Trenches from each recovery well were sloped to the remediation building where groundwater collected in a sump.

When the sump filled, water was pumped into the oil/water separator and free product would then go to a product holding tank. Water from the separator was sent through an air stripper where the majority of volatiles were removed. These vapors were exhausted into the air without further treatment. Monitoring of the vapors was necessary to measure the efficiency of the air stripper and to provide D.C. Environmental Division with records regarding air quality emissions. Treated water from the air stripper was then sent through two (2) granular activated carbon (GAC) canisters to remove any residual. A discharge line carried the treated water to a sanitary sewer, as granted by the District of Columbia, Division of Public Waterworks, Pretreatment Division.

# GROUNDWATER REMEDIATION SYSTEM

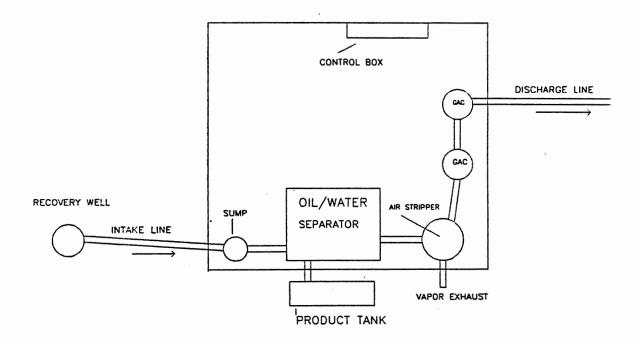


Figure 29. Groundwater Remediation System

#### Risk Assessment

In order to provide a risk characterization to the engineers and contractors at the case study site, it was necessary to use publications on gasoline and actual monitored exposure. If personal or ambient monitoring were conducted at the study site, a site specific risk would be attainable. However, the conditions encountered at the case study site are very similar to those researched providing relevant results and conclusions. This chapter is a culmination of research papers to date. The risk assessment is a multi-step process in which:

- Chemicals at the UST site are identified and indicator chemicals are selected;
- Potential exposure pathways are characterized;
- Human intakes are estimated; and
- Toxicity is evaluated and risks are characterized.

#### Removal Process

The UST removal process consists of seven phases:

1) Breaking and removing of the concrete pads, 2) Removal of gasoline, 3) Excavation of soil above and beside the UST, 4) UST purging, 5) Tank removal, 6) Soil excavation, and 7) Tank disposal.

Contractors used jackhammers to break up the concrete pad above the gasoline underground storage tank. The pad was broken into large squares, approximately 4' x 4'. A backhoe

operator would then use the teeth of the bucket to rip up the concrete, most of the time reinforced with rebar. The backhoe was used to load the larger concrete pieces onto a truck. The concrete was taken to a cement company for reuse. This process varies between two and four hours.

The second phase involves removing the contents of the UST. A hand-pump was most commonly used for the transfer of gasoline into a five gallon bucket. A laborer then took the bucket full of gasoline and poured the contents into an appropriate 55 gallon drum. This cycle continued until all pumpable product had been removed.

The third phase was the soil removal above and along the sides of the underground storage tank. During this phase, the soil was monitored for hydrocarbon contamination. At all underground storage tank removals, contaminated soils were encountered. Even if the integrity of the tank was high, practices of overfilling have been the source of gasoline in the gravel pack and soil adjacent to underground storage tanks.

When enough soil had been removed, to allow the removal of the UST, phase four began. Carbon dioxide, either in compressed gas bottles or dry ice, was used to decommission the tank of explosive flammable vapors. An explosive meter was used to measure the explosive levels and levels in the tanks. When it was safe, the tank was removed. During this phase all people involved were exposed to high levels of organic vapors.

The fifth phase was the removal of the UST from the pit with a backhoe. Before the tank was removed, all pipes leading to the tank were unconnected and the fill pipe removed. Most UST's have a metal loop on the top, allowing the removal with the assistance of a chain and backhoe. This step seems to be easy, but it is very dangerous, since residual product and vapors leave the tank explosive.

Soil excavation was the sixth phase and the amount removed was dependent on the degree of soil contamination. Gasoline vapors were strong and the exposure varied with the proximity of the tank pit. Gasoline contaminated soils were piled on polyethylene sheeting for treatment at another location. A minimum of (2) two soil samples were obtained two feet below the bottom of the tank pit.

Tank disposal was the seventh and final step in the UST closure. A laborer used a high pressure steam cleaner to remove residual product from the inside of the tank. After cleaning, the pieces of metal were hauled off to the scrap yard.

## Selection of Chemicals for Evaluation

The composition of gasoline vapors consists of alkanes, isoalkanes, cycloalkanes, alkenes and aromatics (MacFarland et al, 1984 ). Further detail lists the following compounds: pentane, n-hexane, heptane, octane, nonane, benzene, toluene and trimethyl benzene ( Shamsky and Samimi, 1987 ). In choosing indicator chemicals, the toxicity of the constituents were evaluated. Benzene was first chosen since it is recognized as a human hematotoxin and leukemogen. Two more indicator chemicals, toluene and xylene, were chosen since they are also aromatics and data was more readily available. The purpose of indicator chemical selection is to identify those chemicals which pose the greatest danger to public health.

## Exposure Assessment

This exposure assessment identifies known and potential pathways of gasoline exposure as well as the various routes of exposure, the exposed population and the expected BTX vapor concentrations from each exposure. Research provided exposure monitoring of UST workers by personal monitoring and ambient monitoring. Benzene exposure via personal air samples were collected using 3M 3500 Organic Vapor Monitors with sampling times ranging from 15 minutes to 6.5 hours ( Kramer, 1989 ). In one article, five tank removal sites were surveyed and at each site, breathing zone and general air samples were taken using 400/200 mg ( jumbo ) charcoal tubes ( Shamsky and Samimi, 1987 ). This risk assessment assumed a "worst-case" scenario. Different exposure levels were found between the contractors and the engineer. As a worst case scenario, data generated by personal samples from the contractor and laborers was used.

In this study, ingestion was deleted as a potential source of exposure and inhalation and dermal contact were examined.

## Exposure Pathway Analysis

As described in the SPHEM, the necessary elements of an exposure pathway are sources of contamination, a transport medium, routes of exposure and human receptors at exposure points. The gasoline vapors at UST sites , have all the elements for analysis of contaminate pathways, and these elements are described in the following sections.

Identification of Exposure Sources. Sources of potential exposure to gasoline was present in 5 phases of the UST removal process. These potential exposure sources are summarized in Table III. It was noted that the release mechanism in all sources involved volatilization and dermal contact. This reduced exposure routes to those associated with the release mechanism. The first potential source was the volatilization and dermal contact by the removal of gasoline from the underground storage tank. The second potential source of exposure was by vapors emitted from contaminated soil during excavation. UST purging of vapors was the third potential source of exposure. If groundwater was encountered during excavation, free product and dissolved product was present in the groundwater providing a fourth source. The final and fifth source of gasoline exposure was during the underground storage tank disposal. Residual product in the tank was the source of vapors during, cleaning, cutting and hauling.

## TABLE III

Potential <u>Release Sources</u>	Release <u>Medium</u>	Release Mechanism	
Gasoline removal from UST	Air product	Volatilization Dermal contact	
Contaminated Soil	Air	Volatilization	
UST purging	Air	Volatilization	
Contaminated groundwater	Air Product	Volatilization Dermal contact	
UST disposal	Air Product	Volatilization Dermal contact	

#### POTENTIAL EXPOSURE SOURCES

Identification of Exposure Routes. Routes of exposure discussed in this risk assessment were inhalation and dermal contact. From Table III, these were the primary routes of exposure from the release mechanisms. Ingestion was deleted since human intake of groundwater was not a process or a possibility when removing an underground storage tank. The constituents of gasoline in this study, benzene, toluene and xylene, are aromatic compounds. These compounds are highly volatile. All potential release sources provide exposure to workers through volatilization. Inhalation was the major exposure route for these vapors.

Aside from vapors, volatile chemicals may be inhaled in the form of particulates if the material is subjected to wind-blown transport. This was true for soil contaminated particulates during the soil excavation phase.

Direct contact of human skin with contaminated soils, gasoline, and contaminated groundwater could allow constituents to be absorbed through the skin. The sources for dermal absorption are documented in Table III. Dermal adsorption is a completed pathway of exposure and it was further considered in the risk assessment because of this factor.

Pathway Analysis Summary. The summary of the pathway analysis is shown in Table IV. Complete pathways ( those with pathway, route and exposed population ) were identified for the inhalation pathway near the pit and from dermal contact with soils and groundwater in the tank pit. The groundwater pathway is complete for inhalation and dermal contact only. As previously mentioned, ingestion is not a feasible or complete pathway to UST contractors and engineers.

#### TABLE IV

Release/ Transport Medium	Exposure Point	Pathway Route	Complete
Groundwater	Tank pit	Inhalation & Dermal	Yes
Air	Tank pit & UST	Inhalation	Yes
Soil	Tank pit	Inhalation & Dermal	Yes

#### MATRIX OF POTENTIAL EXPOSURE PATHWAYS

## Estimation of Exposure Concentrations

The most accurate information about exposure is provided by monitoring data. Previous research has provided gasoline exposure concentrations, which were used in this study.

<u>Inhalation</u>. Personal and ambient monitoring data was obtained in a previous study (Kramer, 1989) for gasoline exposures of UST contractors during tank removals. Table V represents BTX vapor concentrations in the excavation and removal of gasoline tanks. The data was generated from a survey of five gasoline removal sites and represents the highest exposure levels encountered in the study. Since this research seeks a "worst-case scenario", this data was used.

#### TABLE V

## BTX VAPOR CONCENTRATIONS IN THE EXCAVATION OF USTS

Compound	Avg. Conc. (PPM)	Range	8hr. TWA
Benzene	13.5	0-116	3.50
Toluene	27.2	0.1-230	7.08
Xylene	18.8	0-150	4.90

<u>Dermal</u>. Direct skin contact with gasoline gave the highest levels of exposure. Assuming zero dilution of product, the exposure concentrations were derived from the percent of each constituent. Table VI below represents BTX percentages ( Hadler et al, 1986 ).

#### TABLE VI

## BTX PERCENTAGES IN GASOLINE

Compound	ક	PPM
Benzene	2.2	22,000
Toluene	3.1	31,000
Xylene	0.9	9,000

## Estimation of Human Intake

Human intakes of benzene, toluene and xylene were calculated for each exposure route, inhalation and dermal contact.

Inhalation. Standard human intake coefficients as provided in the SPHEM were assumed in intake calculations. For benzene the average daily intake was calculated at 5.7 mg/kg/day. The Lifetime Average Daily Exposure (LADE) for cancer risk assessment is 4.5E -04 mg/kg/day. The unit cancer risk of this exposure for 70 years is 1.17E -05.

For toluene the 8 hour TWA was 7.08 ppm or 21 mg/m<sup>3</sup>. The daily intake would be 6 mg/kg/day. The calculation is shown below.

For xylene the 8 hour TWA value was 4.90 ppm or 14.7 mg/m <sup>3</sup>. The daily intake would be 4.2 mg/kg/day. The calculation is shown below.

$$\frac{14.7 \text{ mg } x 20 \text{ m}^{3} \text{ x}}{\text{m}^{3} \text{ day}} \frac{\text{z} \text{ m}^{3} \text{ x}}{70 \text{ kg}} = 4.2 \text{ mg/kg/day}$$

Dermal. The dermal uptake was calculated by multiplying the absorption rate by the concentration of the contaminant and then multiplied by the exposure time. All this is divided by the body weight and the average lifetime. The following dermal uptake was calculated:

benzene : 4.45E -11 mg/kg/day
toluene : 5.12E -10 mg/kg/day
xylene : 4.31E -10 mg/kg/day

Total surface area of arms and hands of 0.312 m  $^2$  was assumed.

## Risk Characterization

Characterization of health risk of contaminants was assumed to be additive, as recommended in the SPHEM. Exposure concentrations were compared to Occupational Safety and Health Administrations (OSHA) criteria and were evaluated for these additive risks. Comparisons of projected levels for noncarcinogens, and between calculated risks and target risks for potential carcinogens, provide the final estimate of health risks from BTX vapors at UST sites. Specific health risks were computed for each route of exposure and then combined to determine the total risk posed by the site.

Noncarcinogenic Health Risks. Noncarcinogenic risks or health hazards were developed through the hazard index as described in the SPHEM. The hazard index was calculated from the summation of the ratio of a projected intake to a reference dose for each selected chemical. Additive effects, as shown by a hazard index greater than unity, may indicate a potential health risk at a specific exposure point. Table 5 compares the daily intake of each chemical vs. the acceptable daily intake.

## TABLE VII

## DAILY INTAKE VS. ACCEPTABLE DAILY INTAKE

compound	daily intake	acceptable daily intake	ratio
Toluene	6	0.771	7.8
Xylene	4.2	4.0E -01	10

Carcinogenic Health Risk. Potential carcinogenic risks were developed using the daily intake multiplied by the carcinogenic potency factor for benzene. Benzene is classified by the EPA as "A", known human carcinogen. Carcinogenic potency factors were obtained from the SPHEM and route specific risks were calculated. Total risk was the summation of the specific risk for each exposure source. The unit risk from inhalation exposure was 1.17E -05 and the risk from dermal contact was computed at 4.45E -11 . The total carcinogenic risk for UST site is 1.17E -05 .

## Discussion of Health Risks

The risk characterization of working at a gasoline underground storage tank removal indicates both noncarcinogenic and carcinogenic risks are not within generally accepted values. The total carcinogenic risk from benzene was 11 cancers per one million people exposed. This is slightly higher than acceptable. Another method for comparison is OSHA's benzene standard of 1.0 ppm (8-hr TWA). Previous studies as well as this paper has found benzene exposure to be unacceptable. Please refer to Table V where the 8 hour TWA was arithmetically calculated at 3.5 ppm.

For the noncarcinogenic risks, acceptable daily intakes were compared to 8 hour TWA daily intakes for toluene and xylene. Table VII shows that the daily intakes for both compounds were extremely high when compared to the acceptable daily intakes. The ratio of daily intake by acceptable daily intake ranged from 7.8 to 10. This is most definitely unacceptable.

With these conclusions it is important to state that the worst case scenario was assumed in every step of the assessment. The highest concentrations of exposure came from laborers in the pit and when cleaning the tank prior to disposal. These two phases of work do not represent levels found across the site or by all personnel at the site. Unit risk is overestimated since most people will not be exposed 8 hours a day, 40 hours a week, for 70 years.

However, the daily intake concentrations in comparison to acceptable intake concentrations is very significant. There are also many sites where exposure to large concentrations of gasoline vapors can be for many days. This is a health risk, that should be addressed especially under these possible extenuating circumstances. Venting is recommended at these unusual sites with extraordinary circumstances.

## CHAPTER VII

## DISCUSSION

The investigated site in the case study did not provide enough data for a detailed review of site characterization and corrective action procedures. This chapter discusses site characterization and corrective action procedures for a leaking UST in Oklahoma for the year 1991-1992. Rule 13, Corrective Action Requirements, from the <u>Oklahoma</u> <u>Corporation Commission General Rules and Regulations</u> <u>Governing Underground Storage Tanks in Oklahoma</u>, gives specific site characterization and corrective action procedures. Details and support guidance for this rule can be found in the <u>Guidance Documents and Checklists for</u> <u>Indemnity Fund Applications</u>, prepared by Staff, July 18, 1991.

## Initial Response

Upon confirmation of a UST release, there are three (3) initial response actions that must be conducted by owners and/or operators within 24 hours. The following responses must be conducted:

- Report the release to the Oklahoma Corporation Commission (405/521-3107) or the Department of Pollution Control on a weekend (800/522-0206);
- 2. Take immediate action to prevent any further release of the regulated substance into the environment; and
- Identify and mitigate any fire, explosion, and vapor hazards.

Initial Abatement Measures and Site Check

The next step is to initiate abatement measures and gather data from the site check. During this process, owners must perform the following measures:

- Remove enough of the regulated substance from the UST to prevent further release;
- Visually inspect the release and prevent further migration of the released substance;
- Continue to monitor and mitigate any additional fire and safety hazards;
- Remedy hazards posed by exposed contaminated soils. If disposal was performed, include state, city and county permits, if applicable;
- 5. Confirm the release, by sampling, if necessary; and
- Investigate the presence of free product and begin free product removal as soon as practical.

After conducting the above measures, the owner must submit a report to the Commission, within 20 days after release

confirmation, summarizing initial abatement steps.

Initial Site Characterization

The Initial Site Characterization (ISC) is conducted to confirm the release, what type of contamination is present and how the contamination has affected the soil and/or groundwater. The characterization gives general information as well as the geology and the hydrogeology of the site. The ISC must include, but is not necessarily limited to, the following:

- Data on the nature of the material released, how the release occurred, and the estimated quantity released. Inventory data and reconciliation is one source of data, estimates of the quantity of product found is another;
- Data on the surrounding populations that might be effected;
- 3. Regional water quality;
- The use and locations of water wells within one mile of the site;
- 5. Regional and site subsurface conditions. Provide contoured soil contamination plume map(s) and cross sections. Regional subsurface soil conditions can be determined by using available documents from Soil Conservation Surveys, USGS, Oklahoma Geological Survey, Oklahoma Water Resources Board, and Oklahoma

State Department of Health;

- 6. Location of all subsurface utilities and the potential zones of high permeability on a scaled map. Several methods include utility maps, surveys, legal records, geophysical surveys, and physical excavation if necessary;
- 7. Climatological conditions from the NOAA (National Oceanic and Atmospheric Administration) and information on the average monthly rainfall, lumens and temperature;
- 8. Land use within a half mile of the site, including a brief description of the use. This adjacent property study may provide additional sources of contamination;
- 9. Depth to groundwater measurements on site;
- 10. Groundwater sampling for BTEX and TPH. Contoured free product, groundwater contamination plume map(s) and cross sections if sufficient data is available;
- 11. Results of the site check; and

12. Results of free product investigations.

All the above data must be submitted in the Initial Site Characterization Report within 45 days of release confirmation. The report will also include analytical data sheets, tabulations, chromatograms, evaluation of all analyses, previous reports and references. If soil and groundwater contamination exceeds OCC standards then a Site Characterization, investigation for soil and groundwater clean up, must be conducted.

Site Characterization

A Site Characterization, Investigation for Soil and Groundwater Cleanup (Rule 13.06), must be conducted for sites with both soil and groundwater contamination. The Site Characterization determines the source of the contamination, the horizontal and vertical extent of the contamination, the geology and the hydrogeology of the site. This Site Characterization Report (SCR) should be cumulative of all previous reports, data, and field notes. The information gathered and conclusions drawn from this report will provide the information necessary to design and implement an effective Corrective Action Plan (CAP).

The site characterization must accomplish the following:

- 1. Adequately define subsurface stratigraphy;
- Provide complete descriptions and accurate interpretation of the data;
- 3. Soil and groundwater contamination plume maps that identify the full extent of soil and groundwater contamination;
- Groundwater contour maps must establish direction of groundwater flow and flow paths;

- 5. Determine the actual or potential impact of the contaminant on site structures and wells;
- Proper groundwater monitoring well design and diagrams that provide an accurate assessment of the saturated zone;
- Determine the volume of gasoline released into the environment;
- 8. Status of UST's at the facility; and
- 9. Resolve any gaps of missing data.

The owner/operator of the leaking UST must develop and submit to the Commission, a Site Characterization Report (SCR) that includes the following:

- 1. Table of Contents, Executive Summary and Report Introduction:
- 2. Site history
  - study adjacent properties and contact previous land owners
- 3. Site maps
  - site vicinity map
  - topographic map
  - utilities and pertinent site features
  - soil boring/monitoring well location map
- 4. Soil
  - soil contamination contour map
  - soil boring logs
  - soil sampling
  - plugging soil borings
- 5. Groundwater
  - groundwater contour maps
  - groundwater contamination contour map
  - monitoring well designs
  - groundwater sampling
  - plugging monitoring wells
  - hydrogeologic cross sections

- Free product evaluation

   free product contour map
- 7. Extent of contamination
- 8. Analytical data sheets
- 9. Hydraulic conductivity
   - apparent water velocity
   - porosity
- 10. Environmental impact evaluation
- 11. Remedial alternatives

### Site History

The site history review must include the entire UST history of the site, including when and how the contamination was discovered, when it was reported, initial actions taken, and estimated quantity of product lost including inventory reconciliation. A title review should be conducted on the property and previous owners should be contacted and questioned about previous land use. Aerial photographs at the Oklahoma Geological Survey provide an historical land use study of the property and the adjacent properties. Federal, state, and local government agency files should be reviewed for previous land use, fires, hazardous materials, spills, etc.

# Site Maps

There are several items to be addressed in the site map(s). The site map should be accurately scaled depicting the site and surrounding area. Show the location and content of existing and removed USTs, product lines and dispensers, pertinent site features (i.e., buildings, roads, water wells, oil and gas wells, oil field facilities, water ways, sinkholes, tile lines and/or sewer lines, etc.), the location of soil borings and monitoring wells, location of utility lines at the site, adjacent property boundaries and potential adjacent sites. A site vicinity map should be on a topography map developed from work done at the site, USGS maps, city, or Area Council of Government Surveys.

# <u>Soil</u>

Assessment of the soil at a UST site will be conducted by providing a contoured soil contamination plume map. This map will depict the full extent of soils exceeding OCC soil clean up levels and the levels of contamination within the plume. Soil boring logs should accompany the report. The borings should be drilled into the uppermost zone of saturation. The soil boring log must include the following information:

- 1. The driller's name;
- 2. Drilling method and bit/auger size;
- 3. Date started and finished;
- 4. Hole identification;
- 5. Hole location, elevation, and total depth;
- 6. Gross petrography (soil and/or rock types) of each geologic unit;

- 7. Soil description using a recognized description method (i.e., Unified Soil Classification System, Burmister, or percentage of each component);
- 8. Thickness of soil zones/layers, and the areal extent of each;
- 9. Depth and location of any contaminants encountered in the boreholes;
- 10. Sampled interval and depths at which samples were obtained;
- 11. Geologic and other pertinent observations; and
- 12. Screened interval.

It is necessary to discuss the qualifications of the individual who logged the borings, the drilling method, what actions were taken to prevent cross contamination and the basis for which the location and number of borings placed at the site were chosen.

Proper soil sampling is critical for an accurate assessment. The soil sampling discussion must include the following:

- The type of gas (vapor) analyzing (screening) equipment used and how it was utilized;
- The criteria/ rational used to determine the sampled interval and depths at which samples were obtained;
- 3. Sampling methodology (i.e., auger spinup, split spoon, etc.);

- Chain of custody procedures. Provide a copy of the completed chain of custody forms;
- 5. Sample preservation procedures;
- 6. Analytical procedures. The analytical methodology must be a recognized EPA method or some modification of an EPA method. Soil samples must be analyzed for benzene, ethylbenzene, toluene, xylene (BTEX) and for total petroleum hydrocarbons (TPH).

All soil borings shall be plugged or completed as monitoring wells the same day as drilled. Oklahoma Water Resources Board Rules and Regulations, chapter 9, covers this topic.

# <u>Groundwater</u>

Based on work conducted at the site, develop a groundwater contour map of the site indicating the direction and gradient of groundwater flow. Correct the observed water level elevations for any free product. If free product is present, develop a free product contour map. Provide a description of groundwater flow and discuss any anomalous water levels. Describe any fluctuations in the water level, especially if it may alter the general groundwater gradient or flow directions.

The groundwater contamination contour map should depict the full extent of contamination exceeding the OCC groundwater clean up levels; differentiate the levels of contamination within the plume. Correct any groundwater elevations for free product.

During the installation of monitoring wells, the spacing must be close enough together to accurately portray soil and/or bedrock stratigraphy. Discuss the drilling method; actions taken to prevent cross contamination; monitoring well development procedures; the basis used to determine the location and number of monitoring wells placed at the site; and the methodology used to determine groundwater levels. Measurements of both depth to static water level and total depth of the wells must be taken. Water levels must be measured in each well at intervals until the level stabilizes. Static water levels should be measured to the nearest 0.01 foot. Be sure to identify the device used to obtain depth measurements. Detailed monitoring well logs with construction design must be provided with the following information:

- Identification, diameters, (inner and outer) lengths of construction materials, and the outer diameter of the borehole. Monitoring well screens are required to be factory fabricated. State the well screen slotting size, the filter pack material type and size, the type of backfill, and seal(s).
- In plugging an abandoned well, the upper portion of the borehole shall be sealed to prevent infiltration from the surface. Include construction details for all wells.

- 3. How sections of casings and screens are connected, the methods of cleaning well component materials prior to installation, how the filter pack was installed, and how the seals were installed.
- 4. Place a benchmark at the site for all vertical measurements. Ground level elevations and top of casing (TOC) elevations should be measured to the nearest 0.01 foot. Horizontal locations of borings and monitoring wells should be measured to the nearest 0.5 foot. The benchmark will be located on all site maps.

Groundwater samples obtained at the UST site must be conducted under QA/QC procedures. In the SCR discuss the sampling methodology and measures taken to prevent cross contamination (i.e., disposable bailers, designated bailers, decontamination, etc.). Include sample preservation and chain of custody procedures. As with soil samples, provide a copy of the completed chain of custody forms. If conducted, discuss the use of duplicates, spiked or blank samples for quality control. Discuss the analytical procedures. The analytical methodology must be a recognized EPA method or some modification of an EPA method. Groundwater samples must be analyzed for benzene, ethylbenzene, toluene, xylene (BTEX) and for total petroleum hydrocarbons (TPH). When abandoning a monitoring well, the owner is responsible for ensuring that all monitoring wells and borings are abandoned and plugged according to Oklahoma Water Resources Board standards. OWRB Rules and Regulations, chapter 9, covers this topic.

Data gathered from the soil borings and monitoring wells will be used to generate hydrogeologic cross sections. Develop stratigraphically correlated hydrogeologic cross sections or three dimensional diagrams which adequately define spatial relationships of subsurface materials. The cross section or diagram should include the following:

- Identification of the types and characteristics of the geologic materials present;
- Identification of the contact zones between different geologic materials, noting zones of high permeability or fracture;
- 3. Detailed borehole information including borehole location, depth of termination and the depth to the zone of saturation, and water table levels corrected for free product (if any); and
- 4. Vertical and horizontal scales.

A narrative description of the site geology should be included. Compare this data to data obtained through the USGS, OGS, Soil Survey and other agencies.

# Free Product Evaluation

If free product is discovered, discuss the method used to identify the presence of free product and how the free product is being addressed. OCC requires owners to remove as much free product to the maximum extent possible. Free product removal must be conducted in a manner which minimizes the spread of contamination to uncontaminated zones. Handle flammable products in a safe manner. A free product removal report (Rule 13.05) must be submitted to the department within 45 days of discovering free product. The following information must be provided:

- The name, address, and telephone number of the person(s) responsible for implementing the free product removal measures;
- The estimated quantity, type and thickness of free product measured in wells, boreholes, and excavations;
- 3. The type of free product recovery system used;
- The location of any on site or off site discharge during the recovery operation;
- 5. The type of treatment applied to, and the effluent quality expected from, any discharge;
- The steps that have been or are being taken to obtain necessary permits for any discharge; and
- 7. The disposition of materials removed from the site including the recovered free product.

A contoured free product map should be developed and included in the Site Characterization Report.

# Extent of Investigation

If the soil and/or groundwater contamination extends to the property boundary(ies), it is necessary to extend the soil and groundwater investigations to adjacent properties. This should determine the extent of the contamination. If adjacent property owners will not provide access, contact the OCC.

# Analytical Data Sheets

The Site Characterization Report (SCR) must include analytical data sheets from the laboratory, as well as tabulations, chromatograms and the evaluation of all results. The analytical data must be evaluated for Quality Assurance and Quality Control. Spiked or blank samples are critical for this determination.

### Hydraulic Conductivity

Determine the hydraulic conductivity of the subsurface materials, apparent water velocity, water table/piezometric gradient and porosity. Discuss how the porosity was determined (i.e., cores, assumed, etc.). Discuss the methodology used in obtaining the above data (i.e., slug tests, pumping test, etc.). Be sure to show the relevance of the information obtained if it is to be used in pump and treat remediation plans.

# Environmental Impact Evaluation

The SCR must include an evaluation of the actual or potential impact of the contamination to waterwells, residences, buildings, etc. The contaminant's affect on human health and the environment will determine clean up goals, remedial alternatives, public acceptance, and the urgency for remediation.

# Remediation Alternatives

Do not develop a detailed remediation plan until the OCC has reviewed and approved the SCR. Remediation alternatives that require site specific information may be presented and discussed.

# Free Product Removal

Free product removal is detailed in Rule 13.05 of the OCC Rules and Regulations Governing Underground Storage Tanks. The methods used to check for free product and the requirements are the same as previously discussed in Site Characterization, free product evaluation. In summary, the owner must: 1) conduct free product removal, 2) abatement of free product, 3) safely handle flammable and explosive products, and 4) submit a free product removal report within 45 days after confirming a release.

# Corrective Action Plan

At any point after reviewing the information from the 1) initial response, 2) initial abatement measures and site check, and 3) the initial site characterization, OCC may require additional information or a corrective action plan for contaminated soils and groundwater. The owner is responsible for submitting a corrective action plan that provides for adequate protection of human health and the environment as determined by the Commission, and must modify its plan as necessary to meet this standard. The commission will approve the corrective action plan after considering the following factors:

- The physical and chemical characteristics of the regulated substance, including its toxicity, persistence, and potential for migration;
- The hydrogeologic characteristics of the facility and the surrounding area;
- The proximity, quality, and the current uses of nearby surface water and groundwater;
- The potential effects of residual contamination on nearby surface water and groundwater;
- 5. An exposure assessment; and
- 6. Any information or data about the site.

Upon approval of the corrective action plan by the Commission, the owner must implement only these measures approved, including modification of the plan made by the Committee. The owner must monitor, evaluate and report the results of implementing the plan in accordance with a schedule and format set by the Commission.

In the interest of minimizing environmental contamination, the owner may initiate clean up of the soil and groundwater before the corrective action plan is approved. Under this option the owner must:

- Notify the Commission of intention to begin clean up;
- Comply with any conditions imposed by the Commission, including halting clean up or mitigating adverse consequences from clean up activities; and
- 3. Incorporate these self-initiated clean up measures in the corrective action plan that is submitted to the Commission for approval.

# Public Participation

For all UST sites that require a corrective action plan, the owner must provide notice to the public, especially those members of the public directly affected by the release and the corrective action plan. The notice may be provided through notice in local newspapers, block advertisements, public service announcements, publication in a state register, letters to individual households, or personal contacts by field staff. The Commission ensures that site release information and decisions concerning the corrective action plan are available to the public for inspection upon request.

The Commission may hold a public meeting to hear comment son the proposed corrective action plan if there is sufficient public interest, before approving a plan. If the approved corrective action plan does not achieve the established clean up levels, the Commission will consider plan termination.

# CHAPTER VIII

# SUMMARY AND CONCLUSIONS

Groundwater is a valuable drinking water resource in the United States in both availability and quality. Due to the nations large dependence on groundwater as a natural resource, it is critical to protect this resource. One of the largest sources of groundwater contamination comes from underground storage tanks systems (UST's) across the nation. There are several million UST systems in the United States and hundreds of thousands of these UST's, including their piping, are currently leaking and contaminating soil and groundwater. The Office of Underground Storage Tanks, a part of the EPA, has implemented a ten year phase in period of UST's to better protect human health and the environment from their releases.

At many UST sites, initial site characterizations are not conducted in enough detail. This error has lead many remedial designs to be ineffective and do not reach their cleanup goals. When free product is encountered, a true product thickness in the formation should be conducted and addressed in the remedial design. Many times, the volume of product released is estimated and the volume of groundwater

149

necessary to be treated is calculated. At this point, many designs only address treatment of groundwater and forget treatment of the contaminated soil.

The risk posed to the contractors and engineers at UST removal sites is not considered by most planners. Depending however, on the concentration levels of gasoline vapors at a site, the risk can often exceed OSHA's standards for benzene, a known carcinogen.

After detailed research of UST systems and the case study of an industrial site, the following conclusions are listed:

- Detailed initial site characterizations are needed for effective remedial designs.
- A site specific understanding of the subsurface at a leaking UST site, leads to reasonable cleanup goals to be set by a regulatory agency.
- It is important to address residual gasoline contamination in the unsaturated zone as well as the saturated zone.
- 4. Early discovery and containment of any suspected UST leak should occur as soon as possible, so that recovery procedures may be initiated and the influence of any release can be minimized.

- 5. Corrective actions that are potentially applicable to soils contaminated with gasoline include excavation and disposal, enhanced volatilization, incineration, soil vapor extraction, soil washing/extraction and microbial degradation.
- 6. Corrective actions applicable to gasoline contaminated groundwater include air stripping, carbon adsorption, biological treatment and treatment trains.
- 7. All available technologies for soil and groundwater remediation should be evaluated for technical effectiveness, acceptability of the method (clean up goal) and the cost due to specific conditions.
- 8. If only the volume of groundwater necessary to be pumped and treated is considered in remediation, residual contamination will be ignored and the site will not be effectively cleaned.
- 9. In pump and treat systems, lowering of the water table causes gasoline to be smeared across more soil, increasing the amount of sorbed contaminants.
- 10. In situ technologies such as soil venting, biological treatment and soil washing/extraction can effectively treat residual contamination.

- 11. Treatment trains effectively treat contaminated groundwater, but treatments for the contaminated soils should work in conjunction with the groundwater treatment.
- 12. A pre-flush treatment of 10 g/l of NaCl before use of surfactants greatly enhances the oil recovery of soluble hydrocarbons in contaminated soil.
- 13. Witconol SN 70 (alcohol ethoxylate) is the most effective commercial surfactant in a soil washing/extraction process.
- 14. In the promising field of bioremediation, the use of hydrogen peroxide requires pilot studies to establish the amount to be used since it is expensive.
- 15. The characterization of risk from gasoline exposure to contractors and engineers indicates both noncarcinogenic and carcinogenic risks are not within generally accepted values. Venting is recommended at sites where OSHA's benzene standard of 1.0 ppm (8-hr. TWA) is exceeded.
- 16. In the dose-response assessment, extrapolation of animal data to human data for risk characterization creates a large factor of uncertainty for the Risk Assessment process.

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APPENDICES

# APPENDIX A

# SAMPLING AND PRESERVATION PROCEDURES

# FOR DETECTION MONITORING

Parameter	Recommended Container <sup>b</sup>	Preservative	Maximum Holding Time	Minimum Volum Required for Analysis
	Indicators of Gr	ound-Water Contaminatio	<sup>m</sup> c	
рН	T, P. G	Field determined	None	25 ml
Specific conductance	T, P, G	Field determined	None	100 ml
TOC	G. amber. T-lined cap <sup>e</sup>	Cool 4°C. <sup>d</sup> HCl to pH <2	28 days	4 x 15 m1
TOX	G, amber, T-lined septa or caps	Cool 4°C, add 1 ml of 1.1M sodium sulfite	7 days	4 x 15 m1
	Ground-Water	Quality Characteristics		
Chloride	T. P. G	4°C	28 days	50 ml
Iron Manganese Sodium	T. P	Field acidified to pH <2 with HNO <sub>3</sub>	6 months	200 ml
Phenols	G	$4^{\circ}C/H_{2}SO_{4}$ to pH <2	28 days	500 ml
Sulfate	T, P, G	Cool. 4°C	28 days	50 ml
	EPA Interim Drin	king Water Characterist	ics	
Arsenic Barium Cadmium	т, Р	<u>Total Metals</u> Field acidified to pH <2 with HNO <sub>3</sub>	6 months	1,000 ml
Chromium Lead Mercury		Dissolved Metals 1. Field filtration	6 months	1.000 ml

TABLE 4-1 SAMPLING AND PRESERVATION PROCEDURES FOR DETECTION MONITORING<sup>a</sup>

Chromium			0 10/11/15	1,000 mi
Lead		Dissolved Metals		
Mercury		1. Field filtration		
Selenium		(0.45 micron)		
Silver	Dark Bottle	2. Acidify to pH <2 with HNO <sub>3</sub>		
Fluoride	Т. Р	Cool, 4°C	28 days	300 ml
Nitrate/Nitrite	T, P, G	4°C/H <sub>2</sub> SO <sub>4</sub> to pH <2	14 days	1,000 ml

(Continued)

161

#### TABLE 4-1 (Continued)

#### SAMPLING AND PRESERVATION PROCEDURES FOR DETECTION MONITORING

Parameter .	Recommended Container <sup>b</sup>	Preservative	Maximum Holding Time	Minimum Volum Required for Analysis
Endrin Lindane Methoxychlor Toxaphene 2.4.0 2.4.5 TP Silvex	T. G	Cool. 4°C	7 days	2.000 ml
Radium Gross Alpha Gross Beta	P, G	Field acidified to pH <2 with HNO <sub>3</sub>	6 months	1 gallon
Coliform bacteria	PP, G (sterilized)	Cool, 4°C	6 hours	200 m1
	Other Ground-Water Characteristics of Interest			
Cyan 1 de	P, G	Cool, 4°C, NaOH to pH >12. 0.6 g ascorbic acid <sup>f</sup>	14 days9	500 ml
011 and Grease	G only	Cool, 4°C H <sub>2</sub> SO <sub>4</sub> to pH <2	28 days	100 ml
Semivolatile. nonvolatile organics	T, G	Cool, 4°C	14 days	60 m 1
Volatiles	G. T-lined	Cool, 4°C	14 days	60 ml

# <sup>a</sup>References: <u>Test Methods for Evaluating Solid Waste - Physical/Chemical Methods</u>. SW-846

(2nd edition, 1982).

Methods for Chemical Analysis of Water and Wastes. EPA-600/4-79-020. Standard Methods for the Examination of Water and Wastewater, 16th edition (1985).

<sup>b</sup>Container Types:

P = Plastic (polyethylene)

G = Glass

T = Fluorocarbon resins (PTFE, Teflon<sup>®</sup>, FEP, PFA, etc.)

PP = Polypropylene

#### (Continued)

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#### TABLE 4-1 (Continued)

#### SAMPLING AND PRESERVATION PROCEDURES FOR DETECTION MONITORING

<sup>C</sup>Based on the requirements for detection monitoring (§265.93), the owner/operator must collect a sufficient volume of ground water to allow for the analysis of four separate replicates.

<sup>d</sup>Shipping containers (cooling chest with ice or ice pack) should be certified as to the 4°C temperature at time of sample placement into these containers. Preservation of samples requires that the temperature of collected samples be adjusted to the 4°C immediately after collection. Shipping coolers must be at 4°C and maintained at 4°C upon placement of sample and during shipment. Maximum-minimum thermometers are to be placed into the shipping chest to record temperature history. Chain-of-custody forms will have Shipping/Receiving and In-transit (max/min) temperature boxes for recording data and verification.

<sup>e</sup>Do not allow any head space in the container.

<sup>f</sup>Use ascorbic acid only in the presence of oxidizing agents.

<sup>9</sup>Maximum holding time is 24 hours when sulfide is present. Optionally, all samples may be tested with lead acetate paper before the pH adjustment in order to determine if sulfide is present. If sulfide is present, it can be removed by addition of cadmium nitrate powder until a negative spot test is obtained. The sample is filtered and then NaOH is added to pH 12.

# APPENDIX B

# OTHER INDUSTRIAL WASTE LANDFILLS

#### ACTIVE

### OTHER INDUSTRIAL WASTE FACILITIES (OIW)

### April, 1990

### CADDO COUNTY

Public Service Company P.O. Box 201 Tulsa, Oklahoma 74012 Bonnie Hill, Environmental Spec. (918) 590-2760 Frank A. McGilbra, Manager, Environmental Compliance (918) 599-2000

NE4, S4, SW4 of Section 3, 7N, 11W and SW4, NW4, NW4 of Section 10, 7N, 11W adjacent to Washita community.

Permit #3508020 - SOUTHWESTERN STATION - Issued 4/23/84. Surface disposal; Total retention basin.

#### CARTER COUNTY

Custom Service, Inc. P.O.Box 217 Ardmore, Oklahoma 73402 Tommy Harris, Owner (405) 226-7696

SW4 of Section 3, N2, N2, NW4, NW4 of Section 10, 4S, 1W, LM.

Permit #3510015 - Issued 1/10/86 for life. Waste: Uniroyal's wastes only, including asbestos.

Total Petroleum, Inc. Bypass 142 P.O. Box 188 Ardmore, Oklahoma 73402 Patrick E. Binkley, P.E. Environmental Engineer (405) 223-0535

S/2, N/2, NW/4 of Section 16, 4S, 2E

Permit #3510014 - CATALYST LANDFILL - Issued 9/5/85, expires 9/5/88.

#### CREEK COUNTY

International Metal Company (IMCO) P.O. Box 1070 Sapulpa, Oklahoma 74066

Tom W. Rogers, Sr. Vice President Jim McCaskey, Plant Supervisor (918) 224-4746

SW4, NE4, NW4, NE4 of Section 26, 18N, 11E

Permit #3519017M - Issued 8/6/85, for life. Waste: aluminum slag, magnesium slag, and salt cakes. Type IV.

#### GARFIELD COUNTY

Union Pacific Resources Company (formerly Champlin Petroleum) P.O. Box 7 Ft. Worth, Texas 76101-0007 Bruce Hodgen, Site Manager Davis L. Scharff, Staff Super. (405) 234-9706 John Rector (817) 877-7013

SW4, NW4 of Section 3, 22N, 7W, LM.

Permit #3524005 - Issued 4/2/86, for life. Refinery closed, but landfill is active; cleaning up oily sludge and solid waste. Land application system.

### GARVIN COUNTY

Continental Oil Company 3535 N.W. 53rd Street Oklahoma City, Oklahoma D.W. Matthews

SW4, SE4, SW4 of Section 14, 1N, 1E

Permit #3525007 - Issued 7/18/77.

#### KAY COUNTY

Conoco, Inc. 1000 S. Pine P.O. Box 1267 Ponca City, Oklahoma 74603 Bill Bridwell, Chief Envir. Eng. Dennis Parker Brad Bronkaw R.L. Thurstonberg (405) 767-2500

SW4 of Section 3, 25N, 2E

Permit #3536012 - Issued 4/22/86, for life. Waste: asbestos, pipe insulation, calalyst, sludge, stabilize soil.

Grand River Dam Authority (GRDA) Ron Coker, General Manager P.O. Box 409 Vinita, Oklahoma 74301-0409

Pierre Fredrich, Env. Super. Mike Rozell, Asst. Env. Super. (918) 256-5545

Ash Disposal Site: SW4, NE4 and the SE4, NW4 and the N2, NW4, SE4 and the N2, NE4, SW4 of Section 28, 20N, 19E, LM.

Permit #3549012 - Issued 1/31/81, for life. Waste: fly ash.

Coal Pile Runoff Basin: W2, SE4, NW4 and the E2, SW4, NW4; Waste Water Holding Basin: W2, SE4, NW4 and the E2, SW4, NW4; Emergency Overflow Basin: SW4, NW4 and the N2, NW, NW of Section 28, 20N, 19E, I.M.

Permit #3549014 - Issued 1/28/81, for life. Waste: surface impoundments.

Oklahoma Ordinance Works Authority Gene R. Redden, Administrator Mid America Industrial Park (918) 825-3500 P.O. Box 945 Pryor, Oklahoma 74362

SW4 of Section 9, 20N, 19E, LM.

Permit #3549026 - OOWA LANDFILL - Issued 10/15/87, expires 10/15/93. Waste: paper sludge.

SE4, SW4, and the W2, SW4, SE4 of Section 10, 20N, 19E, LM.

Permit #3540011 - MID-AMERICA INDUSTRIAL DISTRICT LANDFILL - Issued 11/24/80.

Protein Technologies International, Inc. Bob Stubblefield (formerly Ralston Purina) (314) 982-3789 Jack Parker, Plant Manager P.O. Box 248 Pryor, Oklahoma 74362 (918) 476-5825

LOCATION: Due East off Hunt Street

Permit #3549016M - Issued 1/25/88, expires 1/25/2008. Waste: biological; land application system.

Pryor Foundry, Inc. P.O. Box 549 Pryor, Oklahoma 74362 Jack Gilbreath, Manager (918) 476-8321

E2 of Section 16, 20N, 19E

Permit #3549024 - Issued 9/30/86. Waste: foundry

#### Muskogee Environmental Conservation Co. 928 N. York, Suite 30 Muskogee, Oklahoma 74403 W.F. "Bill" Scriminger, President (918) 683-2811

SE4, NE4, SW4 of Section 25, 16N, 19E, I.M.

Permit #3551003 - FT. GIBSON - Issued 5/9/86; for life. Waste: fly ash.

SW4 of Section 27, 13N, 17E, LM. (between old Hwy 69 and new Hwy 69)

Permit #3551012 - OKTAHA LANDFILL - Issued 6/24/85; for life. Waste: fly ash.

### NOBLE COUNTY

Evans & Assoc. Construction Co.,Inc. Dale R. Zehr, President P.O.Box 30 Ponca City, Oklahoma 74602

NW4 of Section 8, 24N, 3E

Permit #FA3552008 - Issued 3/13/86; expired 7/31/86.

Oklahoma Gas and Electric P.O. Box 321 Oklahoma City, Oklahoma 73101

Lester Buress, Supervising Environmental Engineer (405) 272-3245 David Branke, Senior Environmental Engineer Control Specialist (405) 272-3690

E2, SE4 of Section 14 and W2, SW4 of Section 13, 23N, 2E

Permit #3552012 - GRASSY POINT LANDFILL - Issued 8/1/88; for life (30 yrs.) Waste: Asbestos only

#### PITTSBURG COUNTY

McAlester Army Ammunition Plant McAlester, Oklahoma 74501-5000 Darrell Elliott, Chief Environmental Management

(918) 421-2551

SW4 of Section 12, 4N, 13E

Permit #3561009 - Issued 2/12/86; for life. Waste: Construction and demolition.

SW4 of Section 30, 4N, 13E, and SE4 of Section 25, 4N, 12E

Permit #3561014 - Issued 7/7/88; for life (7/7/98).

on deposit. Grand River Dam Authority (GRDA) P.O. Box 409 Vinita, Oklahoma 74301-0409

Ron Coker, General Manager Pierre Fredrich, Env. Super. Mike Rozell, Asst. Env. Super. (918) 256-5545

Permit #C/D 3549020 - Issued 12/16/83. Final closure inspection on 5/13/88. No waste applied. Clean closure. No monitoring required. No post-closure bond o deposit.

#### McCURTAIN COUNTY

Weyerhaeuser Company P.O. Box 1060 Hot Springs, Arkansas 71902 James Odendahl, Manager Environmental and Regulatory Affairs (501) 624-8569

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Permit #3545005 - Issued 10/17/83. One time disposal, never applied. Closed clean 4/89. No monitoring required. Post-closure bond, \$50,000 on deposit.

#### MUSKOGEE COUNTY

Muskogee Environmental Conservation Co. W.F. Scriminger, President 928 N. York, Suite 30 Muskogee, Oklahoma 74403

Permit #3551008 - Porum Landfill - Closed 9/19/83. No inspection reports. No postclosure bond on deposit.

### OTTAWA COUNTY

**B.F. Goodrich** 

N2, SE4 of Section 23, 28N, 22E

Permit #3558014 - Closed.

Eagle-Picher Industries, Inc. Boron Plant P.O. Box 798 Quapaw, Oklahoma 74363 Don Short, Supervisor (918) 673-2201 Jan Tupper, Consultant (417) 624-5703

Closure approved 11/17/87. No final closure certification / inspection. No post-closure bond on deposit.

# UNPERMITTED SITES

Foundry Sand Dumping: (per Harriett Muzjlakovich)

Acme Blackwell, Inc. 400 E. Frisco Blackwell, Oklahoma

Electron Corporation 510 N. 25th Street Blackwell, Oklahoma

VITA ----

### Brent M. Ward

Candidate for the Degree of

Master of Science

# Thesis: LEAKING UNDERGROUND STORAGE TANKS: SITE CHARACTERIZATION, REMEDIATION AND RISK ASSESSMENT

Major Field: Civil Engineering

Biographical:

- Personal Data: Born in Marlow, Oklahoma, May 18, 1960, the son of Gene Ray and Barbara Ward.
- Education: Graduated from Western Heights High School, Oklahoma City, Oklahoma, May 1978; received Bachelor of Science Degree in Geology from the University of Oklahoma, Norman, Oklahoma, December 1983; received a Certificate in Hydrogeology from Oklahoma State University/Metro Tech, June 1989; completed the requirements for Master of Science Degree at Oklahoma State University in May 1992.
- Professional Experience: Petroleum Geologist, 101 Energy Corporation, July 1984 to July 1985; Consulting Geologist, KSH, Inc., July 1985 to July 1987; Research Technician, Oklahoma University Health Sciences Center, August 1987 to June 1989; Project Manager, ATEC Environmental Consultants, June 1989 to September 1990; Manager of Environmental Operations, 101 Energy Corporation, September 1990 to December 1991.