PROCEEDINGS

TECHNICAL ASSISTANCE TO U.S. EPA REGION IX: FORUM ON REMEDIATION OF WOOD PRESERVING SITES

October 24-25, 1988, San Francisco, California

Coordinated by

PEI Associates, Inc. 11499 Chester Road Cincinnati, Ohio 45246

Contract No. 68-03-3413 Work Assignment No. 19-1M and 20-1G PN 3741-19-1M and 3741-20-1G

> Technical Project Monitors Edwin F. Barth and John E. Matthews

U.S. ENVIRONMENTAL PROTECTION AGENCY

Risk Reduction Engineering Laboratory 26 West Martin Luther King Drive Cincinnati, Ohio 45268 and Robert S. Kerr Environmental Research Laboratory P.O. Box 1198 Ada, Oklahoma 74820

March 1989

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Field Experience with the KPEG Reagent - Alfred Kornel, EPA-RREL, Cinci., OH	
In-Situ Biodegradation of Organic Pollutants in Groundwater - Dr. C. Herbert Ward, Rice University, Houston, TX	
Onsite Bioremediation of Wood Preserving Contaminants in Soils - Dr. Ronald C. Sims, EPA-RSKERL, Ada, OK (Utah State	University)
Existing Data on Wood Preserving Waste Incineration - Donald A. Oberacker, EPA-RREL, Cinci., OH	
Pump-and-Treat Technology - Dr. Joseph F. Keely, Ground-Water Quality Consultant, Po	ortland, OR
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Groundwater Contaminants at Wood Treatment Facilities - Jeffrey K. Rosenfeld, EPA-EMSL, Las Vegas, NV (Lockho	eed Engineering)
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Appendix A -	Supplementary Material For Overview of the Wood Dr. Gary D. McGinnis, Mississippi State University	Preserving Industry, , MS			
Appendix B -	Supplementary Material For Field Experience with the Alfred Kornel, EPA-RREL, Cincinnati., OH	he KPEG Reagent,			
Appendix C -	Supplementary Material For In-Situ Biodegradation Groundwater, Dr. C. Herbert Ward, Rice University	of Organic Pollutants in y, Houston, TX			
Appendix D -	Supplementary Material For Onsite Bioremediation of Contaminants in Soils, Dr. Ronald C. Sims, EPA-R (Utah State University)	of Wood Preserving SKERL, Ada, OK			
Appendix E -	Supplementary Material For Pump-and-Treat Techn Keely, Ground-Water Quality Consultant, Portland,	ology, Dr. Joseph F. OR			
Appendix F -	Supplementary Material For In-Situ Soil Washing ar Technologies Thomas C. Sale, CH2M Hill, Denver,	nd Flushing CO			

LIST OF SPEAKERS

Name

Dr. Robert B. Ambrose, Jr., P.E. EPA-ORD, Athens, GA

Edwin F. Barth, P.E. EPA-RREL, Cincinnati, OH

Frank J. Freestone EPA-ORD, Edison, NJ

Dr. Walter E. Grube, Jr. EPA-RREL, Cincinnati, OH

Dr. Joseph F. Keely Ground-Water Quality Consultant Portland, OR

Alfred Kornel EPA-RREL, Cincinnati, OH

Dr. Gary D. McGinnis Mississippi State University, MS

Donald A. Oberacker EPA-RREL, Cincinnati, OH

Jeffrey K. Rosenfeld EPA-EMSL, Las Vegas, NV (Lockheed Engineering)

Thomas C. Sale CH2M Hill Denver, CO

Dr. Ronald C. Sims RSKERL, Ada, OK (Utah State University)

Dr. C. Herbert Ward Rice University, Houston, TX Work/Research Interests

Exposure assessment modeling.

Research & technical assistance in stabilization of hazardous waste.

Treatment of excavated oils, sludges, and sediments.

Contaminated soils & cleanup technologies; soil structures.

Site characterization & review; technical enforcement support; technology transfer/training.

Chemical & biochemical methods to detoxicify halo-organics.

Wood science & technology; biotechnology; groundwater & soil analysis.

High temperature incineration of pesticides and hospital wastes.

Groundwater and soil contamination; monitoring strategies; hazardous waste site investigations.

Oil recovery & in-situ soil washing; hydrogeologic investigations of hazardous waste sites.

Soil transport & fate; in-situ EPAbioremediation; land treatment studies.

Microbial/aquatic physiology; water quality and hazardous materials.

LIST OF ATTENDEES

Name	Address	Phone No.
Dr. Robert B. Ambrose Jr., P.E.	EPA-ORD, College Station Rd. Athens, GA 30613	(404) 546-3130 FTS 250-3130
Edwin F. Barth, P.E	EPA-RREL, 26 West Martin Luther King Dr., Cincinnati, OH 45268	(513) 569-7669 FTS 684-7669
James Basilico	EPA-ORD, 401 M St., S.W., Washington, D.C., 20460	(202) 382-2583
Joanne Benante	EPA-Region IV, 345 Courtland St., N.E., Atlanta, GA 30365	(404) 347-3433 FTS 257-3433
Bert Bledsoe	EPA-RSKERL, P.O. Box 1198, Ada, OK 74820	(405) 332-8800 FTS 743-2011
James Brown	EPA-HQ, 401 M St., S.W., Washington, D.C., 20460	(202) 475-7240
Jeffrey Dhont	EPA-Region IX, 215 Fremont St., San Francisco, CA 94105	(415) 974-0990 FTS 454-0990
David Evans	California Regional Water Quality Control Board, 1440 Guerneville Rd Santa Rosa, CA 95401	(707) 576-2220 .,
Bernard R. Feather	California Dept. of Health Services, 2151 Berkeley Way, Annex 7, Berkeley, CA 94704	(415) 540-2596
Felix Flechas	EPA-Region VIII, 999 18th St., Suite 500, Denver, CO 80202-2405	(303) 293-1669 FTS 564-1669
Frank J. Freestone	EPA-ORD, MS-104, Woodbridge Ave., Edison, NJ 08837-3679 FTS	(201) 321-6632 340-6632
Rene Fuentes	EPA-Region X, 1200 Sixth Ave., Seattle, WA 98101	(206) 442-1599 FTS 454-1599
John R. Gealy	EPA-RSKERL, (Dynamac Corp.), P.O. Box 1198, Ada, OK 74820	(405) 332-8800 FTS 743-2011
Dr. Walter E. Grube, Jr.	EPA-RREL, 26 West Martin Luther King Dr., Cincinnati, OH 45268	(513) 569-7798 FTS 684-7798

LIST OF ATTENDEES (Continued)

Name	Affiliation	Phone No.
James Hansen	EPA-Region IX, 215 Fremont St., San Francisco, CA 94105	(415) 974-7232 FTS 454-7232
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Scott G. Huling	EPA-RSKERL, P.O. Box 1198, Ada, OK 74820	(405) 332-8800 FTS 743-2313
Dr. Joseph F. Keely	Suite 2002, Tanasbourne Mall, 2700 NW 185th Avenue, Portland, OR 97229	(503)645-7556
John Kemmerer	EPA-Region IX, 215 Fremont St., San Francisco, CA 94105	(415) 974-7112 FTS 454-7112
Alfred Kornel	EPA-RREL, 26 West Martin Luther King Dr., Cincinnati, OH 45268	(513) 569-7421 FTS 684-7421
Fran Kremer	EPA-RREL, 26 West Martin Luther King Dr., Cincinnati, OH 45268	(513) 569-7346 FTS 684-7346
Mark Lahtinen	Minnesota Pollution Control Agency Groundwater & Solid Waste Division 520 Lafayette Rd., St. Paul, MN 55155	(612) 296-7775 1
John Lank	EPA-Region IV, 345 Courtland St., N.E., Atlanta, GA 30365	(404) 347-7603 FTS 257-7603
Leo Levinson	EPA-Region IX, 215 Fremont St., San Francisco, CA 94105	(415) 974-7101 FTS 454-7101
Carole A. Lojek	PEI Associates, Inc., 11499 Chester Rd., Cincinnati, OH 45246	(513) 782-4767
John Matthews	EPA-RSKERL, P.O. Box 1198, Ada, OK 74820	(405) 743-2233
Dr. Gary D. McGinnis	P.O. Drawer FP, Mississippi Forest Products Lab, Mississippi State University, MS 39762	(601) 325-3101
Donald A. Oberacker	EPA-RREL, 26 West Martin Luther King Dr., Cincinnati, OH 45268	(513) 569-7510 FTS 684-77510

LIST OF ATTENDEES (Continued)

Name	Affiliation	Phone No.
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Ted Park	California Dept. of Health Services, 5850 Shellmound St., Emeryville, CA 94608	(415) 540-2526
Thomas Pheiffer	EPA HQ-OSWER, 401 M St., S.W., Washington, D.C., 20460	(202) 382-4477 FTS 382-4477
Eydie Pines	EPA HQ, 401 M St., S.W., Washington, D.C., 20460	(202) 475-9759 FTS 475-9759
Mark Piros	California Dept. of Health Services, 2151 Berkeley Way, Annex 7, Berkeley, CA 94704	(415) 540-2529
Jeffrey K. Rosenfeld	EPA-EMSL (Lockheed Engineering), 1050 E. Flamingo Rd., Suite 120, Las Vegas, NV 89119	(702) 734-3211
Thomas C. Sale	CH2M Hill, 6060 S. Willow Dr., Denver, CO 80111	(303) 771-0900
Marion R. Scalf	EPA-RSKERL, P.O. Box 1198, Ada, OK 74820	(405) 332-8800 FTS 743-2011
Dr. Ronald C. Sims	EPA-RSKERL, (Utah State University) P.O. Box 1198, Ada, OK 74820	(405) 332-8800 FTS 743-2011
Ken Wallace	USEPA Federal Building Drawer 10096, 301 South Park Helena, MT 59626-0096	(406) 449-5414
Dr. C. Herbert Ward	Dept. of Environmental Science & Engineering, Rice University, Houston, TX 77251	(713) 527-4086
Ronald G. Wilhelm	EPA HQ-OSWER, 401 M St., S.W., Washington, D.C., 20460	(202) 382-7944 FTS 382-7944

DAY 1		AGENDA	
		Topic	Speaker
7:30		Registration	
8:00		Opening Comments	Ronald G. Wilhelm EPA HQ-OSWER, Washington, D.C.
			John Kemmerer EPA-IX, San Francisco, CA
	I.	INTRODUCTION	
8:15		Overview of the Wood Preserving Industry	Dr. Gary D. McGinnis Mississippi State University, MS
	П.	TREATMENT TECHNOLOGIES	
		A. CHEMICAL TECHNOLOGIES	
9:15		Field Experience with the KPEG Reagent	Alfred Komel EPA-RREL, Cincinnati, OH
10:15		Break	
		B. BIOLOGICAL TECHNOLOGIES	
10:30		In-Situ Biodegradation of Organic Pollutants in Ground- Water	Dr. C. Herbert Ward Rice University, Houston, TX
11:30		Lunch Break	
12:45		Onsite Bioremediation of Wood Preserving Contaminants in Soils	Dr. Ronald C. Sims EPA-RSKERL, Ada, OK
		C. PHYSICAL TECHNOLOGIES	(Utan State University)
1:45		Existing Data on Wood Preserving Waste Incineration	Donald A. Oberacker, EPA-RREL, Cincinnati, OH
2:45		Break	
3:00		Pump-and-Treat Technology	Dr. Joseph F. Keely Groundwater Quality Consultant Portland, OR
4: 0 0		In-Situ Soil Washing and Flushing Technologies	Thomas C. Sale CH2M Hill, Denver, CO
5:00		End Day 1	

DAY_2		AGENDA (Continued)							
		Торіс	Speaker						
8:00		Opening Comments	Ronald G. Wilhelm EPA HQ-OSWER, Washington, D.C.						
		C. PHYSICAL TECHNOLOGIES (Cont'd)							
8:15		Physical Separation for Excavated Soils and In-Situ Vacuum Extraction	Frank J. Freestone EPA-ORD, Edison, NJ						
	Ш.	MONITORING STRATEGIES							
9:15		Groundwater Contaminants at Wood Treatment Facilities	Jeffrey K. Rosenfeld EPA-EMSL, Las Vegas, NV (Lockheed Engineering)						
10:15		Break							
	IV	FATE/TRANSPORT							
10:30		Fate and Transport Modeling of Wood Preserving Contaminants in Surface Water	Dr. Robert B. Ambrose, Jr., P.E. EPA-ORD, Athens, GA						
11:30		Lunch Break							
	V.	CONTAINMENT TECHNOLOGIES							
12:45		Capping Wood Preserving Sites	Dr. Walter E. Grube EPA-RREL, Cincinnati, OH						
1:45		Stabilization/Solidification of Metals in Soils and Sludges	Edwin F. Barth, EPA-RREL Cincinnati, OH						
2:45		Break							
3:00		Slurry Walls, Recovery Walls, Interceptor Trenches, and Grout Curtains	Dr. Walter E. Grube EPA-RREL, Cincinnati, OH						
	VI.	CONCLUSION							
4:00		Roundtable Discussion:	General Participation						
4:45		Summary Comments	John Matthews EPA-RSKERL, Ada, OK						
			Ronald Wilhelm EPA HQ-OSWER, Washington, D. C.						

5:00 End Day 2

INTRODUCTION

INTRODUCTION

Wood preserving operations have contributed to contamination at a number of sites proposed or listed on the Superfund National Priorities List (NPL). The U.S. Environmental Protection Agency (EPA) Region IX office in San Francisco, California requested technical assistance in evaluating remedial alternatives for Superfund sites contaminated by wood preservatives (e.g., creosote). Specifically, Region IX requested that the Robert S. Kerr Environmental Research Laboratory (RSKERL) and the Risk Reduction Engineering Laboratory (RREL) present a technical program evaluating remediation technologies for soils and groundwater containing wood preserving contaminants.

PEI Associates, Inc., in support of RSKERL and RREL coordinated development and presentation of a two-day forum on the status of CERCLA wood preserving sites and on remedial technologies potentially applicable to contaminated soil and groundwater at those sites. A total of forty representatives from thirteen EPA offices, four state regulatory agencies, and five consulting or academic affiliations attended the forum conducted October 24-25, 1988 in San Francisco, California. Chemical, biological, and physical treatment technologies were addressed; monitoring strategies and containment technologies were discussed; and fate and transport of wood preserving contaminants in soil and groundwater were considered.

STATUS OF CERCLA WOOD PRESERVING SITES

STATUS OF CERCLA WOOD PRESERVING SITES

A phone survey was conducted by PEI Associates, Inc. to determine the status of fifty-five CERCLA wood preserving sites either proposed or currently listed on the NPL. Remedial Project Managers (RPM's) from eight EPA regions known to have wood preserving sites were interviewed to determine waste types, environmental media affected, current status, and nature of remediation that has been proposed or implemented at each site. The information from this survey is summarized in spreadsheet form in Figure 1.

EPA Regions III, IV, V, VI, VIII, and IX have the greatest number of CERCLA wood preserving sites. Of these, Regions IV and VI are in the most advanced stages of the Superfund process; most of the sites in these regions have a completed Record of Decision (ROD). The predominant waste types encountered are creosote and pentachlorophenol (PCP); the principal contaminants in creosote wastes being polycyclic aromatic hydrocarbons (PAHs). Some sites also are contaminated with dioxins and metals such as chromated copper arsenate (CCA) and ammoniacal copper arsenate (ACA). These wastes are found to be contaminating both groundwater and soil, and in some cases, surface water, lagoons, and river sediments.

Nearly half the sites surveyed have implemented some type of remediation either temporarily (e.g. containment) or as part of the Remedial Investigation/Feasibility Study (RI/FS) or Remedial Action (RA) phases of the Superfund process. Soil bioremediation including treatment is indicated for one-third of the thirty-two sites that have indicated a proposed remediation; incineration of soil and sludges accounts for another third; and various soil technologies such as excavation and removal, soil washing, and solidification/stabilization make up the difference. In terms of groundwater, pump-andtreat technology accounts for eighty percent of the thirty-one sites for which a proposed remediation has been indicated. However, technologies such as in-situ bioremediation are being considered for groundwater remediation in some cases.

Figure 1. Wood Preserving Sites on the Superfund List

	Ste	Location	Region	Contact	Agenci	r Ph	ene He.	Type of Waste 1	Media 2	Statue	Proposed Remediation 2,3	Implemented Remediation 2,3
Ī	Hocemonice Pand	Westberough, MA	1	Jim Certile	USEPA	(817)	\$73-\$734	Cressile	GWI, SWI, SC	ROD MIS	Dewater and cap ingeon; enable landill	N/A
	Mid-Adamic Wood Preservers, Inc.	Harmont, MD	818	Eric Noviman	USEPA	(215)	687-8236	CCA	GW .	Complete RI 12/00	N/A	N/A
	Southern Maryland Wood Treating	Helywood, MD	H1	Anthony D'Appelone	USEPA	(215)	\$07-7713	creases, PAH, disking	GW, SW, SO	ROD 6/86	Incinerate 80	N/A
	Haventown PCP	Heverland, PA		Richard Waterson	USEPA	(216)	\$07-3166	PCP	GWL SWL SO	Campiete Fil 12/00	Pump GW	N/A
	L.A. Clark & Bons	Spotophania City, VA		Herry Herbold	USEPA	(216)	507-4614	C7004010	GIN, SIN, BO	ROD: SCOVER: GW 1999	Boremediate/bash SO GW mending	N/A
	Adaptic Wand Industries, Inc.	Pertomouth, VA		Sharps Falstala	USEPA	(216)	507-0631	creases. PCP. docine?	10.017.91	NES hat starting	N/A	Removal of sension 1966
	Columnar Wand Pressrena, Inc.	Culeanner, VA		Paulo Bataslar	USEPA	(215)	607-1113	CCA	GW 80	Received by MP1	NZA	N/A
	Sunders Burght Co.	Chuckshuch, VA		Andrew Palastat	USEPA	(215)	\$87-1266	PCP. OCA. doubs: human	000 80 80	Draft state of RES	N/A	N/A
	Received, Inc. CA. Wand Proceeding Divisioni	Richmond, VA		But Brendd	LISEPA	(216)	567-1113	the PCP CCA metals	GW 500 80	RES undeles is seving	M/A	I some employment over the even
	American Concerts, Personals PR	Passanda SI		Jaco Dava	155EPA	14645	347.9643	cianania PCP		Complete Bi 8/84	Bongradets er beharets 60	Relation and anneal in 1985
	Read Mand Personing	the Out. FL	Ň	John Vanna	ISPA	1484	347-5643	creation, PCP7		BOD AN	Researcher 90	Removal 1/10
	Palmette Mand Prototelan	Distant SC	Ň	Miles Marshman	ISEPA	(404)	\$47-3631	CCA. PCP		BOD completed \$787	Solid Stabl. BC: mum and binst Chill	Removal order contem and 1985
	American Constitut, Jacknes Start	Jackson Th	ñ	Danata Managanda	11SEPA	(484)	\$47.7781	Granadia PCP		Complete DEP: BOD ADA	Solidication of SC inducation of studen	Canadan 1992: tanin bashing 1995
	Care For Wood Passada	Familie MC		John Brenheim	UNCA	1444	\$47.7781	CHICA PAN		Complete Al Alla	M/A	Removal 1995
	Column France Ward Barrantes Co.	Whitehouse El	Ň	Manadith Andrews	UNCPA	1444	347.2643	PCP match		BOD BER BA In meteret	inclusion & downton BC. tout motor	
	Konnen Co. Int. Elimente Mart	Elements #C		John L and	LINEPA	4041	547.7003	Contactor PCP matche			MAA	Closed math marks 700
	Kannan Co. Int. Manhalla Blant	Manhadia MC		Badasa Basan	UNCERTA	14845	347.7781		•		•	course source parties into
	Balle Ter in Lands Back Blast	St. Londo Rock MM		Burne Burney	MACA	40.195	104.7700			BIER in underer stands	Ensemble SC summer and he at Child	
	Rollin Tax & Chardeni Daves Start	Ormer ON		feeles Retient	L STATE	19195	ANG. 6410	Bald and be deduction		Newsfating for fit	Comments on promp and ever Gree	des perspesses; secare, 30 secred on sas
	there is a communication of the second	Automatica Alian		Martin Cadava	Mac-4	10101			04,00			N/A
	Man China & China Bark Landara	Marrie Balakters ABM		Charles California	MACA	40143	200-1100		GHC BO	Mark a working percent	ATA	RIA
	D. Basis Reserves Company	Concel and All		Enclosed Concernent	MIRCA.	10123	100.7758	808	04,30	And a second state	Children and the second second second	Incompanies a Demonstration organg
	al reger reper de.	California, and			MACA		200-1100	POP	GRC BU	THE S COMPOSED LINES	GW pumpos well; 50 male containment vall	Campional PA Na SO
	Budertes Machan Cash-ut	Protocold Control Addition		Electron Growing		10.00				HE'S COMPL; NV III (FOUR	Changong a dechage GW; Med-excev, SC	Chan-clony well; Med-monitor GW
	berten Manufact & Deserts de	Brankler Cooler 199		ERIDOR GODINANA	MILLA	(51 a)			01(30	THE S CONTRACTOR 1994		Landarit SO, 1996; purpout GW
	Joseph manager, a weight (a.	and the second s		ElExcell Uncommu		10120	200-1100			HI COMPANIES; 1-5 IN SHOP.	Fumpour GW; excevele SO for diffule tanditi	Service and and burn service in the service se
	Recovered particular (California)			Angela Person	USIOFA	(314)	303-1331		GH, SH, SU	Company for 5 by 1/m		#/A
	Commission of the second	Contraction of the local sector of the local s			LEFA	(217)	100-0707			un comb. even: La eubuch.	N/A	BU removal, ensite storage
	Carter Lee Linner VI.	Manageria, M			USEPA	(a) (a)	383-8318				A	· ·
	Not-South Week Presson	Bone, AN		Law Belinks	USEPA	(214)	535-5/35	CINCOLDID, CUA	GHL 30	NO0 11/06	Stabilize cap & SC; pump and treat GW	Capped
	Technicke week rivering Co.	ICENTINA, IX		Sherrie Fueret	USEPA	(Z14)	000-6/18		GH, SU	u int seine		R/A
	United Contemport	Centre, 1X	VI	Des Williams	USEPA	(214)	000-0710	creation, FGP, disting	GW, SD	ND in progress	Contain sources and treat sole	W/A
				Kableen C'Helly	USEPA	[214]	000-0/10	creation, Frid, mathing	GW, SW, SO	HOO 347	incinerate and cap SO; pump and treat GW	7/A
		Chardina, Au		The Mahee	USEPA	(214)	030-0710		011,30		incinerate SC; pump and teal GW	7 /A
	Reppete Co., and, retaining Plant	Jeannand, 1X		Jan Pendergant	USEPA	(214)	533-6/10	CHECKER, PCP, CCA	GHL 30	HE'S CAR; HOD WHE	Excertile and wath SO; pump and treal GW	#/A
	South Cavetage Week	Heading, TX		Jim Pendergant	USEPA	(214)	433-6706	CHORENE, CCA	GHL 80	NES complete; ROU was	Excittate and wash SO; putty and treat GW	#/A
	Journ Constante Breet	Housen, 1X		Jan Pendergant	USERA	{Z14}	633-6793	C1005000	GWI, SU	NE-S 440; NOD 6/94	thoremediate SO; pump and treat GW	#/A
	Artmood	Cinaha, Alt		Pluth ternell	USEPA	(214)	858-6738	C1006010	GMI, 80	FEFS in progress	W/A	1/A
	Bactaci Union Pacific The Treating	Luante, WY	VIII	Terry Anderson	USEPA	(303)	203-1700	creeses, come PCP	GW, SNI, SO	NOO \$496; RA is progress	Oil recovery, SO weaking, bioreclamation	Banch scale lab testing of technologies
	Brederick Wood Products	Denver, CO		Barry Levene	USEFA	(343)	283-1529	creatio, PCP, some deutra	GWL, 80	NOU in vertexe staget	Incin. Ingoon studges; cabon abearb liquids	N/A
	Noriesa Pale and Tioning	9486 , 411	VIII	Charle Coloniat	USEPA	[408]	449-5414	cree, FCP, FCB, metals, disc	GN, SW, 80	Begin RES wiper. 1046	Herneval program, 1985; dechlorination, 1986	N/A
	Muho Polo Ca.	Secondo, MI	VW.	Siephenie Wallace	USEPA	(488)	448-5414	Creation, PCP	GIV, SHE SO	FIFS to begin SADD	N/A	GW recovery system and SW controls
	Burlegton Horthom, Bomore Plant	Sumore, MT	VIII	Stephanie Wallace	USEMA	{400}	449-5414	creceste, metale	GNY, SW, SO	Drait MFS complete	Remove and landlarm SO, possible incineration	Removal of GW and sludges in 1985
	Lbby Groundwater (Champion International)	LEGY, MT	VIII	Ken Walaco	USEPA	(406)	449-5414	crocscie, PCP, matala, volat.	GW, SW, SO	PB near comp.; ROD 12/98	in-aity bioremediation and landlarming	N/A
	Coast Wood Preserving	UNIA, CA	SK.	Jan Hencon	USEPA	(415)	174-7232	CCA	GHL 90	RES 3/06; ROD 1/09	Extraction trust, GW; defer action on SO	Sivery; extraction; electrochem, trimt.
	Solme Treating Co.	Seime, CA	R.	Roberts Blank	USEPA	(418)	874-6214	PCP, CCA, double, furans	GIV, 80	ROD \$/66; RD is progress	Pemp & Ireal GW; Itration/capping of SO	N/A
	Kappent Co., Int., Cheville Plant	Overfile, CA	CK.	John Kentmorer	USEPA	(415)	974-7112	creaseds, PCP, CCA	GN, SN, SO	Complete RIFS in 1298	Pump & treat GW; wash, blorem, or incin. SO	Vacuum & seal SO is process area, 1987
	Southern California Billion (Visalis)	Visalia, CA	SK.	Joli Chent	USIEPA	[415}	574-0010	creasale, PCP, dissing	GHL 80	INE 2 bendling approval	Carbon absorption of GW	Carbon absorption of GW; SO removal
	J.H. Baster	Weed, CA	氰	Lee Lovineen	USEPA	(415)	974-7191	creaseste, PCP, ACA, distine	GW, SWI, SO	NFS in prog.: ROD 10/80	Pwmp & treat GW; bloram., Incin., or fix 90	French drain in place for GW control
	Louisiana-Pacifit Corp.	Chantle, CA	DK.	John Kennerer	USEPA	(415)	974-7112	PCP, formaldehyde	GNN, SC, deal	NI sear cump.; NOD 1990	H/A	N/A
	Marky Cooling Tower Co.	Stocktom, CA	IX.	Judy Walker	USEPA	(4 18)	974-7615	Creosole, CCA	GNI, 80	She is no longer on the NPL	N/A	N/A
	Valley Wood Preserving, Inc.	Turleck, CA	9 K	Tracy Sillington	USEPA	(8 16)	924-2130	CCA	GW, 80	First phase of AIFS	N/A	N/A
	Wychaff Co./Eagle Histor	Babbridge Sel., WA	X	Lod Cohen	UBERA	(206)	442-2712	cressols, PCP, metals	GW, 80, 9D	RIFS in various staget	N/A	N/A
	Joseph Forest Frederic	Jaseph, CR	x	Kellh Rese	USEPA	(206)	442-7721	CCA	GW7, 80	Fil to start Fall of 1990	N/A	N/A
	American Crossestet & Conduit Co.	Chokalla, WA	x	Les Marshall	USEPA	(206)	442-2723	Creesets, PCP	SD	In Remedial Action phase	incineration on site	N/A
1	Pasce Bastary Landill	Pasce, WA	x	Bob Klevit	USEPA	(206)	763-0014	Posticidos, tar, metala. atc.	GW, SW1, 50	Negoliste Ni in Isla 1960	N/A	N/A
							-			-		

FOOTNOTES

CCA = Charmond Copper Assesse; PM = Polycycle Anomalic Hydrocarbone; PCP = Pontachamphenet; ACA = Annonincel Copper Anonato; PCB = Polychiologiaded Biphonyl
 GW = Groundwater; BM-Bulace water or logene; BCI-Bell or logene andmenet; BCI-Bell or logenet

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FORUM SUMMARY

FORUM SUMMARY

The following presents a brief summary of each speaker's presentation. The technical papers are presented in Section 4 of the proceedings. Handouts, copies of overheads, slides, and other supplementary material corresponding to several speakers are included in the Appendices.

Opening comments were made by Ronald Wilhelm of the Office of Solid Waste and Emergency Response (EPA-OSWER) in Washington, D.C. and John Kemmerer of EPA-Region IX in San Francisco, California. Mr. Wilhelm explained that the forum was developed at the request of Region IX and that the intent was to provide an informal technical workshop for EPA personnel involved in remedial actions at wood preserving sites. Mr. Wilhelm reported that funding for the forum was provided by the U.S. EPA Program Office in support of Superfund Technical Assistance. He also mentioned that proceedings of the forum would be published and used as the basis for development of future technical training and a technical resource document for RPM's assigned to wood preserving sites. Mr. Kemmerer welcomed the attendees of the forum to Region IX and noted that the problem of remediating wood preserving sites was common to all EPA regions. He also thanked Ron Wilhelm, John Matthews of EPA-RSKERL and Carole Lojek of PEI Associates, Inc. for their assistance in bringing the forum to Region IX.

Dr. Gary McGinnis of Mississippi State University presented a brief overview of wood preserving wastes and the wood preserving industry. Dr. McGinnis explained that wood preserving sites in the United States are located geographically in two wood-growing bands: one in the east/southeast, and one in the west/northwest. Wood preservatives are used to prevent microbial degradation and decay from termites and other wood parasites. The most common use of preserved wood is for railroad ties, telephone poles, piers, and other types of construction lumber. Dr. McGinnis explained that chemicals used in wood treating are comprised of two distinct groups: oil-borne or organic wood preservatives (e.g. creosote and PCP), and water-borne preservatives (e.g. copper, chromium, arsenic, and zinc). These chemicals are commonly introduced into the wood in cylinders at high temperatures and pressures. Dr. McGinnis also discussed the environmental media affected (i.e. groundwater, soil, air) and the associated contaminants which are commonly found in these media at wood preserving sites.

Alfred Kornel of EPA-RREL in Cincinnati, Ohio made a presentation on the destruction of chlorinated dioxins, furans, and other halogenated aromatics found in soil and groundwater using chemical reagents prepared from polyethylene glycols and potassium hydroxides (KPEGs). Bench scale tests using these reagents have successfully demonstrated the dehalogenation of polychlorinated biphenyls (PCBs) to less than 1 ppm and chlorinated dibenzo-p-dioxins (PCDDs) and chlorinated dibenzofurans (PCDFs) to less than 1 ppb. Field testing of this treatment technology was initiated in January 1986 at the Montana Pole and Treating site near Butte, Montana. Concentrations of PCDDs and PCDFs (1000 ppm) contained in 9000 gallons of waste oil were successfully reduced to non-detectable levels at this site. Mr. Kornel also summarized field test results using alkali metal polyethylene glycolate complexes (APEG) at the U.S. Navy's Public Work Center in Guam. Approximately 30 tons of soil at this site is contaminated with PCBs (2500-4500 ppm) which resulted from the process of rebuilding transformers and capacitors. Results of field-scale pilot tests indicate PCBs in contaminated soils (600-3000 ppm untreated) at this site were successfully reduced to less than 1 ppm.

Dr. Herbert Ward of Rice University in Houston, Texas spoke about in-situ biodegradation of both soluble and nonaqueous phase organic pollutants in groundwater as applied to wood preserving sites. In-situ biorestoration refers to the stimulation of indigenous subsurface microorganisms using limiting nutrients and oxygen to aerobically degrade organic pollutants. Dr. Ward stressed that successful employment of this process is site-specific and depends on availability of the following factors: adaptive microbes, specific aquifer characteristics, aerobic conditions, electron acceptor (oxygen, peroxide, nitrates), nutrient enrichment, acceptable toxin levels for the microbes. Subsurface microbes characteristically are: very small in size; widely available; highly active; oligotrophic; mostly prokaryotes (e.g. bacteria).; geologically very old; associated with the soil matrix; and randomly distributed. Dr. Ward also reviewed the results of a field study at the United Creosoting Company site in east Texas.

Dr. Ronald Sims of Utah State University, who is currently on sabbatical at the EPA-RSKERL in Ada, Oklahoma, spoke about onsite bioremediation of wood preserving contaminants in soils using various approaches such as land treatment, suficial in-situ, subsurface in-situ, and bioreactors. Dr. Sims listed eleven CERCLA wood preserving sites where some mode of bioremediation has been proposed. Degradation, transformation/detoxification, and immobilization are three key concerns in bioremediation. Dr. Sims explained that bioremediation involves the intermingling of principles from three

disciplines: molecular biology, ecology, and engineering. Molecular biology entails utilizing microbes which display an active and diverse metabolism. Ecology involves the determination of factors that stimulate or limit microbial growth and activity such as pH, salinity, synthetic chemicals, osmotic pressure, radiation, and physiological barriers. Engineering as applied to bioremediation relates to parameters such as toxicity, rate of biodegradation, rate of transport to the groundwater, and characteristics of the breakdown products. Dr. Sims also reviewed results of successful pilot scale studies involving land treatment at the Burlington Northern site in Brainerd/Baxter, Minnesota.

Donald Oberacker of EPA-RREL in Cincinnati, Ohio discussed the applicability of incineration as a remedial technology for wood preserving wastes with the exception of those sites having significant concentrations of heavy metals. Mr. Oberacker presented existing data on four incineration trial burns of wood preserving wastes such as PCPs and creosote. A study conducted for the Department of Defense involving incineration of wooden ammunition boxes treated with PCP resulted in non-detectable levels of dioxins or furans in the stack. Studies conducted for the EPA-Office of Solid Waste (EPA-OSW) involving incineration of PCP and creosote contaminated bottom sediment/sludge from wastewater treatment at the Allied Chemical plants in Alabama and Mississippi resulted in non-detectable concentrations of dioxins, furans, and all priority RCRA volatile and semivolatile compounds in the ash. Stack test results for the Mississippi plant were unavailable, however, verbal reports of stack test results from the Alabama plant indicate non-detectable levels of dioxins or furans. In a series of EPA tests conducted at thirteen facilities, results from one facility, Anderson Windows, where PCP treated wood containing PVC was incinerated, indicated small amounts of dioxins and furans in the stacks and ash. In this case, however, the variability of incinerator chamber temperatures at the facility may have been the cause. Mr. Oberacker also presented a description of hardware and specifications used for mobile/transportable hazardous waste incineration for field site cleanup operations.

Dr. Joseph Keely of Portland, Oregon spoke about the design criteria and operation of pumping well systems as a remedial technology for groundwater at hazardous waste sites. Dr. Keely stressed the importance of optimizing pumping strategies by considering such critical factors as well construction, aquifer conditions, hydrogeology, demographic constraints, and the physiochemical properties of the contaminant (e.g. dispersion, sorption, ion exchange, etc.). A common type of groundwater remediation involves the use of injection and extraction wells to induce stabilization of a contaminant plume. A contaminant plume may be temporarily or permanently immobilized to allow for withdrawal and above ground treatment; to allow delivery and recovery of products and reactants for in-situ subsurface biotreatment; or to allow for future development of newer treatment technologies. Dr. Keely also discussed pulsed pumping vs. continuous operation of an extraction-injection wellfield. Pulsed pumping involves cyclic operating and nonoperating phases of extraction or injection wells. One reason for this pumping strategy is to allow time for diffusion and contaminant movement from low permeability zones to high permeability zones. In addition, rapid flow rates during remediation may not allow time for sorbing compounds to build up to equilibrium concentrations or for non-aqueous phase residuals to dissolve into the groundwater. By allowing time for these processes during the nonoperating phases, pulsed pumping increases the concentrations of contaminated groundwater removed during the operating phases. In closing, Dr. Keely stressed that pump-and-treat technology is not a proven technology but an accepted one and that realistic goals must be set when using this technology.

Thomas Sale of CH2M Hill in Denver, Colorado made a presentation on in-situ soil washing and flushing technologies, including primary and enhanced recovery systems as applied to creosote oils. Primary oil recovery will only recover a fraction of the oil; onethird of the pore space contains oil that can be displaced under waterflooding. This residual oil is very difficult to displace because the interfacial tension between water and oil prevents movement through pore spaces. Primary oil recovery involves pumping fluids through a formation where oil concentrations are above the residual saturation using a fluid recovery system such as wells, trenches, or drain lines. Mr. Sale presented a case study from the Baxter/Union Pacific Tie Treating plant in Laramie, Wyoming. In this field pilot study 10,000 gallons of creosote were recovered from a two feet thick zone using drain line systems at a depth of 12 feet over an area with a 50 foot radius. During a system scale up, 100,000 gallons of creosote were recovered from a two acre area. Mr. Sale stressed that the success of water flooding may be limited by the presence of differential permeabilities due to heterogeneities in the formation, thus the application of primary recovery technology is very site specific. Of the various enhanced recovery methods available to date, only surfactant-assisted flushing can be successfully applied to creosote oil at wood preserving sites. A surfactant is a surface active agent which accumulates along the oil/water interface, reduces interfacial tension between fluids and allows oil to move more readility through a solid formation. Surfactant-assisted flushing combines water flooding technology with the use of surfactants to provide enhanced recovery where oil concentrations are at residual saturation.

Frank Freestone of the Office of Research and Development (EPA-ORD) in Edison, New Jersey talked about physical separation for excavated soils and in-situ vacuum extraction technologies. Physical separation addresses particle size and mineralogical considerations such as the tendancy of an organic to adsorb onto the surface of a grain or into the interstices of a laminar clay. This technology involves the use of a trommel screen or drum washer to separate sands from clays, silts, and humic materials. After separation the sand sized fraction should be clean enough to be replaced on the site, while the finer particles (<25 microns) which contain the vast majority of contamination must be remediated further using some other technology such as incineration. Soil test results from the site of a fuel oil spill at the Naval Air Station in Lakehurst, New Jersey indicated that 99% of the contamination was contained in the finer grained material (<25 microns). In a pilot scale test conducted at this site, sands and clays which initially contained 3.6% oil and grease underwent a 99% removal; only 1% oil and grease remained in the residual soil. Insitu vacuum extraction involves the removal of soil gas by putting a vaccuum on a system of extraction wells, drawing gases through the soil, and subsequently separating the organics out. A program demonstration was conducted at a site in Groveland, Massachusetts where TCE was used as a degreasing solvent and is the principal contaminant in the soil. Four extraction wells and four monitoring wells were installed at the site. After 56 days of soil-gas extraction, there was a substantial reduction of TCE levels in soil gas samples from all four wells. Mr. Freestone pointed out that soil-gas extraction is a viable technique for wastes having a low molecular weight (e.g. TCE) but is probably not applicable to high molecular weight wastes.

Jeffrey Rosenfeld of Lockheed Engineering, which provides technical assistance to the Environmental Monitoring Systems Laboratory (EPA-EMSL) in Las Vegas, Nevada presented a talk on monitoring strategies for groundwater contaminants at wood preserving facilities. Mr. Rosenfeld was involved in a study in which 126 organic priority pollutants in groundwater from five creosote sites across the country were compared. The purpose of this study was to determine organic compounds which are common to the wood preserving industry and to use this information in developing monitoring strategies for these sites. Based on this comparison, the most commonly detected volatiles are simple aromatic compounds and the most commonly detected semi-volatiles include phenolic compounds and PAHs which are the two major constituents of creosote. Further analysis of these results indicate that concentrations of these compounds are determined by four factors: solubility, adsorption, chemical reaction, and biodegradation. Mr. Rosenfeld noted the consistency of chemical detection across the five sites and concluded that only 27 of the 126 organic priority pollutants are detected in the groundwater. PCPs, PCBs and pesticides were generally not detected; it is assumed that none of these compounds were extensively used in the wood preserving process at these sites. Likewise, results of a study to determine inorganic indicators (e.g. arsenic, chromium, and copper) for wood treatment sites were inconsistent because inorganics played a very small role in the preserving

process at these sites. In summary, a monitoring strategy for wood treatment sites should emphasize the semi-volatile compounds, and also the highly mobile volatiles. It is also important to know the type of process used at the site to determine whether metals should be monitored. Teflon or stainless steel casing is recommended for wood treating sites; PVC should not be used since there is potential for organic compounds to degrade or to react with the material. Groundwater sampling should be done at the top of the aquifer to monitor floaters, but it may also be necessary to sample at the bottom of the aquifer to monitor sinkers such as creosote.

Dr. Robert Ambrose of the Office of Research and Development (EPA-ORD) in Athens, Georgia addressed fate and transport modeling of wood preserving contaminants in surface water. Mr. Ambrose conducted a risk assessment to estimate the risk of PCP entering surface water due to drippage from a wood drying site. The models for this assessment were based on laboratory and field data from Heath Creek, an actual location near Rome, Georgia. Three chemical pathways in a surface water system were modeled: contaminant loading to the stream; upstream flow dilution; and bioaccumulation. Contaminant loading to the stream was modeled using an unsaturated zone model called PRISM. This model was used to predict water pathways, sediment pathways, and pollutant leaching in terms of average loads of runoff, erosion, and leaching. Upstream flow dilution was modeled using the pesticide root zone model which calculates stream concentration due to erosion, runoff, and leaching. The food and gill exchange of toxic substances model (FGETS) was used to predict the bioaccumulation in the fish. FGETS is a dynamic model which looks at daily changes in water concentration, and the change in the weight of the fish versus time (fish growth). Based on the results of this modeling, the average concentration of PCP in a sculpin fish over the course of its lifetime was determined to be 24 ppb. When this fish was fed to a trout to simulate the food chain effect, the whole body concentration running average of the trout was measured at 43 ppb; without the food chain effect this concentration was 40 ppb. All of these results are well below the drinking water standard for PCP (220 ppb).

Dr. Walter Grube of EPA-RREL in Cincinnati, Ohio made a presentation on capping or cover systems as a remedial technology at wood preserving sites. Dr. Grube reviewed several publications which are useful reference guides in the design, operation, and maintainence of cover systems for CERCLA and RCRA hazardous waste sites. Cover systems are used primarily in humid climates for the prevention of precipitation and infiltration. In more arid climates, cover systems are intended to provide protection against burrowing rodents and to prevent radon loss from the underlying wastes at uranium tailings sites. A typical multiple layer cover system includes a barrier soil layer or biotic barrier, a lateral runoff or drainage layer, a vegetative layer, and a foundation layer or traffic surface. Dr. Grube stressed the importance of quality control/quality assurance in the construction phase of cover system design. Affects of freeze and thaw conditions on the integrity of compacted clay soil must be considered. The performance and integrity of a multilayer system having surficial structures such as monitoring wells must be evaluated. Compatibility tests must be conducted on liners to determine if leachate on the compacted soil will undergo physical or geochemical alteration that may compromise the liner integrity. As an example of the wide acceptance of multilayer cover systems, Dr. Grube presented a hazardous waste landfill in Hamburg, West Germany where experimental cover designs are incorporated into the actual remedial cover. Monitoring gas collection, infiltration and leachate collection are also conducted at this site.

Edwin Barth of EPA-RREL in Cincinnati, Ohio discussed the applicability of stabilization/solidification (or immobilization/fixation) technology to metals in soils and sludges at wood preserving sites. Solidification is the process of converting a non-solid to a solid; this process does not necessarily prevent leaching. Stabilization involves a chemical reaction such as precipitation, complexation, and organic binding which is used to decrease leaching. Stabilization/solidification (S/S) technology is advantageous to many other technologies because it is relatively inexpensive and has gained public acceptance. In general, lead, nickel, zinc, copper, cadmium, chromium III, and low-level organics may be better stabilized than arsenic III, arsenic V, chromium VI, mercury, and high-level organics. However, each unique soil matrix will dictate the feasibility of stabilization. It is important to note that the presence of sulfates, nitrates, phenols, and oil & grease will interfere with the S/S process. Mr. Barth reviewed the soil characteristics which impact S/S, the variables and types of leaching/extraction tests to use, and the various physical tests that S/S is subjected to. S/S technology may be applicable to wood preserving sites contaminated with copper and chromium but may be less effective for wastes containing arsenic and PCP. There are currently some CERCLA wood preserving sites which are evaluating S/S as a remedial technology. Mr. Barth presented data from a S/S pilot study conducted at the Whitehouse, Florida Superfund site. Organic material in soil at this site was stabilized with an organophilic clay. After stabilization, soil analysis using the Toxicity Characteristic Leaching Procedure (TCLP) resulted in non-detectable concentrations of four semi-volatile compounds.

Dr. Walter Grube of EPA-RREL also presented an overview of containment technologies such as slurry walls which are being used at some wood preserving sites. A slurry wall is a positive impervious barrier which is constructed to interface with a natural impervious layer or aquitard thereby preventing further migration of leachate. In constructing the slurry wall, a trench is dug with a backhoe and a bentonite/water suspension is introduced in order to maintain the open ditch. Ultimately the ditch is backfilled with an impervious or low permeability barrier usually obtained by mixing the bentonite from the slurry trench with soil excavated out of the trench. Geomembranes can be also be used in conjunction with the soil/bentonite backfill mixture. Slurry walls are typically proposed at hazardous waste sites which have a high groundwater table, highly unconsolidated pervious soils, a sufficient groundwater gradient to drive the pollutants; and a groundwater sink such as a river, pond, or ocean. As part of their remedial technology, wood preserving sites may be "boxed in" with slurry walls designed to reduce groundwater inflow and to hold the contaminants on site. In most remedial designs a slurry wall is constructed to contain the contaminant area for improved efficiency of a treatment process being applied; its use is typically not meant to be a permanent solution. Dr. Grube reviewed an example of slurry wall technology at the Gilson Road-Sylvester Site in Nashua, New Hampshire. At this site, the slurry wall system includes 4000 feet of slurry wall, recovery wells to pump the groundwater, and recharge trenches to reinject the treated material.

At the conclusion of the presentations, an informal roundtable discussion was conducted to provide a forum for additional concerns and questions which were not addressed during the talks. Summary comments were made by John Matthews and Ronald Wilhelm. Mr. Matthews expressed his gratitude for having the opportunity to provide technical transfer on the remediation of wood preserving sites to the Regional EPA offices. He thanked the individuals from EPA Headquarters, the Technology Centers at the EPA-ORD Laboratories, and PEI Associates, Inc. who were involved in the combined effort to present the forum. Mr. Matthews also mentioned that proceedings from the forum would be compiled and distributed to all attendees. Thomas Pheiffer of EPA-OSWER in Washington, D.C. requested that the attendees provide him with feedback on the forum so that funding for additional technical transfer programs can continue to be made available. Ronald Wilhelm thanked all the speakers and the regional representatives for attending and reiterated that the material presented during the forum would be used as the basis for a training package for RPMs.

FORUM PRESENTATIONS

OVERVIEW OF THE WOOD PRESERVING INDUSTRY

Dr. Gary D. McGinnis, Mississippi State University

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OVERVIEW OF THE WOOD-PRESERVING INDUSTRY

Gary D. McGinnis Professor of Wood Science & Technology and Chemistry Mississippi Forest Products Utilization Laboratory Mississippi State University Mississippi State, MS 39762-5724

Wood preserving in the United States is a hundred-year-old industry. Wood is treated under pressure in cylinders with one of four types of preservatives: creosote; pentachlorophenol in petroleum; water solutions of copper, chromium, and arsenic; and fire retardants. Because of past practices, many sites have relatively large amounts of sludges, contaminated soil, and in most cases contaminated ground water. This presentation will describe the chemical composition of the organic wood preservatives, the avenues by which these chemicals are getting into the environment, and the current methods used by the industry to clean up contaminated soil, sludges, and ground water. OVERVIEW OF THE WOOD-PRESERVING INDUSTRY

By

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January 1989

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OVERVIEW OF THE WOOD-PRESERVING INDUSTRY

History

For centuries, wood has been treated with various organic and inorganic compounds to make wood last longer against the destructive forces of nature. Various chemical systems have been developed to protect wood from the effects of insects, fungus, marine organisms, fire, chemical degradation, and weather.

Processes for extending the life of wood had been developed before the birth of Christ. The Chinese used salt water to extend the life of wood. Persians and Romans used olive oil on bridge timbers to increase service life. In 1716 a patent was issued to Dr. William Cook to treat ship planking against shipworms and decay with tar oil. In the early nineteenth century, a U.S. patent was issued to Kyan, Burnett, and Bethell for treatment with tar oils. In 1848 the first inorganic salt preservative plant was built to treat timbers for the docks and canals on the Merrimac River in Massachusetts, and in 1865 the first Bethell plant to pressure treat creosote railway material was built. In 1875 the first major plant, and one that is still operating, for treatment of railroad piles, timbers, caps, and ties with creosote was built by the Louisville and Nashville railroad in West Pascagoula, Mississippi. A large number of plants were started in the early 1900's to treat railroad crossties, and by 1930 almost all crossties were treated with creosote before placement in service. A major change occurred in the industry when the chestnut blight of 1915 killed the chestnut trees, the softwood species of southern pine and Douglas fir took over for use as utility poles. A large number of plants were started to pressure treat these materials.

Size and Location

From the beginning the wood-treating industry in the United States has been a relatively simple, low-product cost, small family-owned operation. In the 1930's some of the now larger companies treating with oil preservatives began to emerge, but even today most of the companies are still a one or two plant operation. In the future with the current environmental regulations, many of the small companies will not survive, and the industry probably will be dominated by new and the larger companies. A new company would have a major economic advantage since the plant could be designed so that environmental costs would be minimal and the company would not be liable for the tremendous cost of clean-up of past environmental practices before environmental regulations come into effect.

Figure 1 shows the location of the plants in the United States. In 1978 there were 631 commercial plants in operation; currently, there are considerably fewer due mainly to the cost of environmental clean-up. The majority of plants are located along the eastern seaboard, across the southeastern United States, and in the Pacific Northwest. The majority of sites generally correspond to the forested areas of the United States.



Figure 1. Location of wood treating plants in the United States.

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The Process

The current wood-preserving process used in the United States is primarily for the protection of wood against decay and insects. A small percentage is treated with fire retardants. There are two broad groups of chemicals used to preserve wood--oils and oilborne preservatives and the waterborne preservatives (Table 1). The oilborne preservatives are mainly organic while the waterborne preservatives are mainly inorganic salts.

When logs are brought to the wood-treating plant, the initial step in the wood-treating process involves removing the bark. After debarking, the moisture content of the wood is reduced by air-drying, kiln-drying, or by drying directly in the pressure vessels used to treat the wood with the preservative. This latter technique removes the water from the wood by either steaming the wood in the retort, heating it in oil under reduced pressure, or by exposing it to hot vapors of organic solvents in a process called vapor drying.

After drying the wood is ready to be treated with the wood preservative. Preservative impregnation can be accomplished by either pressure or non-pressure methods. Currently, 95% of all preservative treated wood products are produced using pressure impregnation. The pressure processes typically are done using pressures of 50 to 250 psi depending on species of wood. Preservative temperatures employed during the treating cycle vary with the preservative used. Creosote and its solutions are normally applied at temperatures of 210° to 230° F. The temperature used with pentachlorophenol solutions varies with the solvent and may range from ambient to 220° F. With one exception, all waterborne preservatives are applied at ambient temperature. Creosote Table 1. Chemicals used in wood treatment.

A. Organic Wood Preservatives (Oils and Oilborne Preservatives)

Creosote
Pentachlorophenol (4-8%) in a heavy oil Pentachlorophenol in a volatile solvent

B. Waterborne Preservatives

Combination of copper, chromium and arsenic salts
Combination of zinc, copper and arsenic
Combination of ammonia and metal salts
Combination of dinitrophenol, zinc and other metal salts may be applied in undiluted form or diluted with coal tar or petroleum. Pentachlorophenol is applied in a solvent of low volatility such as a heavy oil or in a volatile solvent such as mineral spirits, methylene chloride. or liquefied petroleum gas.

At the completion of the pressure cycle, a final vacuum is applied to remove most of the free liquid on the surface. The wood is moved from the treating cylinder, generally on railroad tracks, to drip pads where the excess chemicals are allowed to drip onto the ground. In most cases the logs are moved to log storage areas. The purpose of storing logs on log storage areas is not only to provide an inventory of material but also in the case of the waterborne preservatives, to decrease the moisture content and therefore reduce shipping costs.

The type of and relative amount of treated wood products produced in 1978 are shown in Table 2. The major products are railroad ties, poles, and lumber. The major wood preservative is creosote. The oilborne preservatives make up 72% based on volume of products or 81% based on weight of the preservative used. Currently, based on personal observation, the use of the waterborne preservative usage has increased substantially relative to the other two preservatives. This increased use of waterborne preservatives is due partially to environmental considerations. The waterborne preservatives require water as a solvent (in other words are not water users) while the oilborne produce large amounts of sludge as well as contaminated process water. Both of these fractions must be treated before they can be discharged. A more detailed description of the waste produced during wood treatment is given in a later section of this paper.

	Treated With									
Products	All Preservatives ^D	Creosote Sòlutions	Penta	Waterborne Preservatives (CCA/ACA/FCAP)						
		<u>1,000</u> cu	. ft							
Crossties and switch ties ^C	106,085	103,138	449	2,498						
Poles	64,179	18,237	41,905	4,038						
Crossarms	1,685	41.0	1,615	29.1						
Piling	12,090	9,993	1,154	943						
Lumber and timbers	105,305	10,779	21,209	73,317						
Fence posts	20,028	4,584	10,983	4,461						
Other products ^d	18,113	7,815	2,681	7,616						
All products	327,485	154,587 (123.7) ^e	79,996 (40.0) ^f	92,903 (37.2) ^f						

Table 2. Volume of treated wood in 1978 (2).

^aVolume reported for 1978 (AWPA), plus volume reported by respondents to Assessment Team Survey, plus volume estimated for nonrespondents. ^bCreosote, penta, and CCA/ACA/FCAP only. ^cIncludes landscape ties. ^dIncludes plywood.

Note: Components may not add to totals due to rounding. ^eTreating solutions in million gallons. ^fTreating solution in million pounds.

Organic Chemicals Used to Treat Wood (3)

The majority of chemicals used to treat wood are used to preserve wood from decay and insects. Since the oilborne preservatives (organic preservatives) are the major components in this group (Table 2) and because of their greater environmental problems, they will be the only group that will be discussed in this section.

Technical grade pentachlorophenol used for treating wood contains 85 to 90% pentachlorophenol (Fig. 2). The remaining materials in technical grade pentachlorophenol are 2,3,4,6-tetrachlorophenol (4-8%), "higher chlorophenols" (2-6%), and dioxins (0.1%). The tetrachlorophenol is added to pentachlorophenol to increase the rate of solubilization. "Higher chlorophenols" are formed during the manufacturing of pentachlorophenol and consist of two or more fused aromatic rings linked by oxygen or carbon bridges. There are a relatively large number of different "higher chlorophenols" in technical grade pentachlorophenol.

There is approximately 0.1% dioxin in technical grade pentachlorophenol. The dioxin which makes up over 90% of this fraction is octachlorodibenzo-p-dioxin. There are also traces of the hepta and hexa isomers. None of the very toxic 2,3,7,8-tetrachlorodibenzo-pdioxin has been found in pentachlorophenol produced in the United States. Manufacturers of pentachlorophenol in the United States have been able to lower the levels of hexachlorodibenzo-p-dioxins in technical grade pentachlorophenol to the 1 ppm levels recently by modifying their manufacturing processes.


85-90%





4-8%





2-6%

Higher Chlorophenols



≈ 0.1%

(octa-, traces of hepta-, and hexachlorodioxin)

Figure 2. Composition of technical grade pentachlorophenol.

Creosote is an even more complex mixture of chemicals produced from coal by destructive distillation. The major components are polynuclear aromatic hydrocarbons (PAH's). Over 274 individual compounds have been identified in creosote. The concentration and structure of some of the major components found in creosote are shown in Table 3 and Figure 3.

Types of Environmental Contaminations at Wood-Treating Sites

The major sources of hazardous waste from the wood-treating process occurs during the treatment cycle. Oilborne preservatives mix with water to form a contaminated process water. The major source of water is from the wood; smaller amounts come from steam leaks in the treatment system and rainwater. Prior to the environmental rules (before 1970's), the waste water was treated and then sent to surface drainage or a stream. A large number of the plants had sumps or ponds to trap the heavy oil residuals before discharging to a creek or to a public-owned treating works (POTW). Ponds ranged from less than 1 to 4 or more acres. Normally, none of the ponds were lined with anything but the local soils.

Many of the older plants treated the waste water before sending it to ponds using a primary oil/water separator. Flocculation or adsorption of the wood-preserving oils by the addition of clays, resins, alum, lime, or polymers is sometimes used as a secondary wastewater treatment process after primary oil/water separation. Currently, most oilborne plants use both a primary oil/water separation treatment followed by a secondary treatment using polymeric materials to lower the levels of oil in the water. The solid sludge obtained (K001 Hazardous Waste) is shipped to Hazardous Waste Storage Facilities while the water

Creosote component	% Whole creosote		
Naphthalene	17.0		
2-Methylnaphthalene	6.5		
1-Metnylnaphthalene	3.5		
Biphenyl	1.9		
Acenaphthylene	0.5		
Acenaphthene	7.8		
Dibenzofuran	5.2		
Fluorene	6.0		
Phenanthrene	19.4		
Anthracene	2.52		
Carbazole	5.1		
Fluoranthene	11.8		
Pyrene	8.4		
1,2-Benzanthracene/Chrysene	4.2		

Table 3. Major components of creosote (2).

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Figure 3. Structures of the major components of creosote.

can be sent directly to a POTW, or it can be further treated by biological treatment and/or carbon treatment at the wood-treating site and sent to a POTW, or recycled using the water as make-up water for waterborne preservatives.

Although waste water and sludges produced by treatment of the waste water are of major concern to the environmental agencies, they are not necessarily the major environmental problem at wood-treating sites. Most sites have both ground water contamination and large amounts of contaminated soil. Large amounts of contaminated soil are found around and below the ponds (or former ponds) used to store the waste water and sludges. Contaminated soils are also found around the treating cylinders and the track areas due to drippage from the treated material as it is moved from the treating cylinders to storage areas. Another source of contamination is the areas around the storage, treating, and unloading tanks due to minor preservative spillage from broken pipes, bleeding of treated wood, etc. These areas can be rather large, especially in the older railroad and pole plants.

Chemical, Biological, and Photochemical Changes in Wood-Treating Chemicals in the Environment (3-6)

In general, when chemicals are put in the environment, several processes can occur. The sample can undergo decomposition; it can be lost by direct volatilization into the air, or it can migrate through the soil into the ground water. The relative occurrence of each of these processes depends on many factors, including the physical and chemical properties of the chemical, the physical and chemical properties of the soil or water, and other environmental effects (amount of wind, amount and direction of water movement, etc.). At most sites the largest amount of contamination is found in the soil, so the following discussion will be limited to the changes occurring in the soil.

Three major types of decomposition reactions occur in the soil-photochemical, chemical, and microbiological. The photochemical process is initiated by ultraviolet radiation from sunlight. Both pentachlorophenol and creosote are degraded by sunlight, and this reaction is very important in water contaminated with these materials. However, in soil this reaction is much less important since it occurs only at the surface of the soil.

Chemical decomposition in soil or water, such as air oxidation or hydrolysis of weak bonds, is not an important reaction with these two groups of chemicals since they do not have any groups that are easily oxidized or hydrolyzed.

With both creosote and pentachlorophenol, microbiological decomposition is the major process occurring in soil. There have been a large number of studies on the breakdown of pentachlorophenol in soil. Figure 4 summarizes the sequence of reactions that have been shown to occur. In soil, pentachlorophenol undergoes a reversible methylation reaction to form pentachloroanisole, but this reaction apparently is not part of the main decomposition pathway. The main route for decomposition is not through the methyl derivative, but through pentachlorophenol. The route of decomposition involves dechlorination leading to a series of partial dechlorinated products, such as 2,3,5,6tetrachlorophenol. The second general step in the decomposition reaction involves an oxidation step to form substituted hydroquinones or

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Figure 4. Microbiological decomposition of pentachlorophenol.

catechols, such as 2,3,4,5-tetrachlorocatechol. The oxidation product then undergoes ring cleavage, ultimately forming CO₂ and inorganic chloride ions.

The factors that are important on the rate of degradation of pentachlorophenol in soil are organic content of soil, moisture content, clay content, and type of bacteria and its population. Another factor is the oxygen content of the soil. Pentachlorophenol is broken down under aerobic and anaerobic conditions; however, the oxidation step which leads to breakdown to CO_2 and inorganic chlorine is favored by aerobic conditions.

Studies with a variety of soil types (Table 4) have shown that the time for 90-100% breakdown varies from 21 days to 1 year. The one exception was a study where pentachlorophenol was added to sterilized soil in a sealed container. Under these conditions the time estimated for complete degradation was over 5 years.

There are many types of bacteria and fungi that are capable of degrading pentachlorophenol, including <u>Pseudomonas</u>, <u>Aspergillus</u>, <u>Trichoderma</u>, and <u>Flavobacterium</u>. Good sources of these bacteria are areas that have been exposed to pentachlorophenol for long periods of time; for example, soil around telephone poles or around wood treating plants. Regardless of where the soil is obtained, the soil bacterial population capable of degrading pentachlorophenol can be increased by acclimating the soil to ever-increasing amounts of pentachlorophenol.

The major components of creosote are the polycyclic aromatic hydrocarbons (PAH's) with trace amounts of phenols and azaarenes. A wide range of soil organisms, including bacteria, fungi, cyanobacteria (blue-green algae), and eukaryotic algae, have been shown to have the

Degradation parameter	Soil type	Special conditions	Time	
90% degradation	Arable layer in rice fields (11 soils)	60% water 25% water	Approx. 50 days Approx. 30 days	
	Forest red- 60% yellow soil 25% sublayer		No degradation in 50 days	
90% degradation	Wooster silt loam	7.5 kg/ha penta, optimum conditions for microbial growth	Approx. 22 days	
Complete	Dry soil	Sealed in air- tight container	> 5 years	
Effect on growth of corn and cucumbers	Fertile sandy loam	Air-dried Medium water Water saturated	<pre>> 2 months 2 months 1 month</pre>	
90% degradation	Mature paddy soil	Low organic content	1 month	
Complete degradation	Dunkirk silt loam	Aerated, aqueous soil suspension	Approx. 72 days	
Complete degradation	Paddy soil	Soil perfusion	21 days	
Complete degradation	Warm, moist soil		> 12 months	
98% degradation	Permeable soil	Composted with sludge from wood-treating plant	205 days	

Table 4. Degradation of pentachlorophenol in soil (1).

enzymatic capacity to oxidize PAH's. Prokaryotic organisms, bacteria, and cyanobacteria use different biodegradation pathways than the eukaryotes, fungi, and algae, but all involve molecular oxygen. Figure 5 shows one proposed mechanism for the microbiological reaction.

Generally, rates of degradation for PAH compounds decrease as the molecular weight increases; rates of degradation are faster in soil than water; and overall rates of degradation are faster where there is an acclimated bacteria population. Compounds such as naphthalene, phenanthrene, and anthracene, which are readily metabolized, are relatively water soluble, while persistent PAH's, such as chrysene and benzo(a)pyrene, have a lower water solubility. Exceptions exist with pyrene and fluoranthene in that these compounds are more soluble than anthracene and yet have not been found by some researchers to be appreciably metabolized by soil microorganisms. Other factors that may affect the persistence of PAH compounds are insufficient bacterial membrane permeability to the compounds, lack of enzyme specificity, and lack of aerobic conditions.

The fate of PAH compounds in terrestrial systems has been reviewed by Sims and Overcash (5), Edwards (6), and Cerniglia (7). These reviews present additional information on PAH degradation.

Currently, the industry is using a variety of methods to clean up the waste materials at the site. At the present time, most ponds containing KOO1 waste have been removed. The material has been incinerated or sent to hazardous waste storage sites. Work on clean up of contaminated soils and ground water is just getting started and will be a major task for the industry. Currently, most sites are being cleaned up using biological processes. In the case of ground water.



Figure 5. Proposed mechanism for the microbiological degradation of anthracene (4-5).

pump and treat technology and carbon columns have been the most widely used method for clean-up. In the case of contaminated soil, various bioremediation methods have been widely used as well as off-site storage. More detailed discussion of these results will be given in a later section of this proceedings.

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FIELD EXPERIENCE WITH THE KPEG REAGENT

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FIELD EXPERIENCE WITH THE KPEG REAGENT

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ABSTRACT

Chemical reagents prepared from polyethylene glycols and potassium hydroxide (KPEGs) have been demonstrated under mild conditions $(25^{\circ} - 140^{\circ}C)$ to dehalogenate PCBs, PCDDs, and PCDFs with laboratory destruction efficiencies exceeding 99.99992. The reaction mechanism is nucleophilic substitution at an aromatic carbon.

Bench scale studies have already established conditions for PCB destruction to less than 1 ppm and for PCDDs and PCDFs to less than 1 ppb. Toxicological tests have established that arylpolyglycol by-products from KPEG reactions are non-toxic. The non-toxic property of the by-products may allow for delisting and on-site disposal of treated materials. In July and August 1986, a 2700 gallon KPEG reactor was used in Butte, Hontana, on a wood preserving site and in Kent, Washington, on a waste disposal site to successfully detoxify PCDDs and PCDFs (120 ppb - 200 ppm) in 17,000 gallons of liquid waste to non-detectable levels. A reactor designed to treat both liquids and solids has been tested on selected Superfund and Department of Defense sites. These field studies have validated conditions for destruction of PCBs, PCDDs, and PCDFs to acceptable levels required by the regulations. This presentation will review treatment data, regulations for treated materials, costs, and the potentials of KPEG for the destruction of a variety of halogenated pollutants.

INTRODUCTION

Chlorinated dibenzo-p-dioxins (PCDDs), polychlorinated biphenyls (PCBs), and chlorinated dibenzofurans (PCDFs) are three series of related compounds that gained notoriety for their high toxicity and persistence in the environment. In the last few years PCDDs and PCDFs have increasingly been identified in chemical product waste streams as well as in effluents from incineration processes.

Most of our knowledge of PCDDs and PCBs as environmental contaminants is associated with their occurrence in soils, sediments, combustion particulates, and in fish. In most cases, this contamination stems from improper waste disposal of highly toxic PCDDs in such products as hexachlorophene or 2,4,5trichlorophenoxy acid herbicides (2,4,5-T, herbicide orange). The occurrence of PCDDs in fish is considered to be the major source of these compounds in humans. While PCDDs arise principally from dimerization of chlorophenols, PCDFs are primarily produced from pyrolysis of PCBs.

Although the toxicological profiles with aquatic organisms are limited, it has been determined that short-term exposure of fish to low ppb and ppt of PCB and PCDD concentrations respectively, cause decreased growth rate, poor survival and increased mortality. PCDDs, however, are considered to be a probable human carcinogen.

The accumulation of PCDDs, PCBs, and other toxic halogenated compounds in the environment and living systems is a serious problem that has been well documented. Although a great amount of work has been done by many groups on the area of direct chemical decomposition of halogenated organics, relatively little effort has been directed toward on-site chemical detoxification.

The "cleanup" of a contaminated site, which often appears in the news media, is not really a permanent detoxification but rather a transfer of a toxic spill from one region to another. As an example, PCB-contaminated soil along some of the highways of North Carolina has been dug up, and has only been removed, at great expense, to another area of that state and landfilled. These PCBs are still in the environment and will persist there until they are removed and destroyed.

The chemical stability of PCDDs, PCBs, and other haloorganics precludes their destruction by conventional refuse incineration methods. Most municipal incinerators cannot achieve the high temperatures necessary to destroy these chemicals in refuse. The surprisingly high volatilization rates of PCBs and other chlorinated aromatic compounds raises questions over the use of land disposal for these materials.

Currently, some commercial chemical methods are available to chemically alter or destroy PCBs and other haloorganics in contaminated oils. The chemical methods developed by Acurex, Goodyear, and Sun Ohio involved dispersion of metallic sodium in oil or the use of sodium-biphenyl or naphthalene mixtures. Because of the reactivity of sodium with water, some of these reagents cannot be used efficiently to directly decompose PCDDs or PCBs in soils, sludges, sediments and dredgings. Other chemical reactions have been evaluated for dehalogenation of environmental pollutants but have not been found to be adaptable to field conditions (1,2,3,).

Biological treatment of PCDDs, PCBs, and other hazardous pollutants is also receiving attention. The efficacy of microbes to destroy toxic halogenated compounds has not been fully evaluated by U.S. EPA or independent laboratories.

KPEG PROCESS

During the summer of 1978 a new chemical reagent was synthesized and used to effectively dechlorinate PCB-contaminated oils (4). Since that time a series of reagents has been prepared from potassium hydroxide and polyethylene glycol (KPEGs) which, with heating, produce rapid dehalogenation of haloorganic compounds (5,6,7,8).

In the KPEG reagent preparation, potassium hydroxide reacts with polyethyene glycol (molecular weight approximately = 400) to form an alkoxide (see Equation 1). The alkoxide in turn reacts initially with one or more of the chlorine atoms on the aryl ring to produce an ether and potassium chloride salt (see Equation 2). In some KPEG reagent formulations, dimethylsulfoxide (DMSO) is added as a cosolvent to enhance reaction rate kinetics by improving rates of extraction of aryl halide wastes into the alkoxide phase (6).

$$HO PEG + KOE \longrightarrow KO PEG + E_0$$
(1)

$$Aryl-Cl + KO PEG ----> Aryl -O- PEG + KCl$$
(2)

In 1982, detailed investigations were initiated to determine the effects of variable reaction parameters on the rate and extent of chemical decontamination of soils (9). This research focused almost exclusively on the direct chemical treatment of PCDD-contaminated soil. The first field investigation, initiated in January 1986, was aimed at identifying treatment conditions for chemical destruction of PCDDs and PCDFs in oil stored on a wood preserving site in Butte, Montana (10).

PURPOSE

Research and field investigation studies were initiated in January 1986, to determine if a chemical reagent, prepared from potassium hydroxide and polyethylene glycol, could be used to treat PCDD and PCDF contaminated oil at an industrial wood preserving site near Butte, Montana. The wood preserving site contained approximately 9000 gallons of light petroleum oil collected previously from groundwater over a period of two years. The oil contained 3.5% pentachlorophenol, PCDD and PCDF homologs ranging from 422 ppb of tetra-isomers to 83,923 ppb of octa-isomers. Because of the presence of these highly toxic chlorinated dioxins and furans, the oil could not be transported off-site for incineration. Bringing in and operating a mobile incinerator for on-site destruction of contaminated oil was rejected because of high costs. In April 1986, U.S. EPA Region 8 agreed, after a review of laboratory data, that the chemical process, based upon a potassium polyethylene glycol (KPEG) reagent, could be used to decontaminate the PCDD/PCDF contaminated oil on-site.

The mobile field equipment employed to implement the previous chemical process comprises of a 2700-gallon batch reactor mounted on a 45-foot trailer equipped with a boiler/cooling system and a laboratory/control room area. Heating of the raw oily waste/APEG reagent mixture was achieved by the recirculation of the oil and reagent through a pump, a high shear mixer, and a tubeheat exchanger which was heated using a boiler or cooled through a series of fin-type air coolers. A schematic is shown below:



The process was employed in July 1986, to successfully destroy PCDDs and PCDFs (1000 ppm) in 9000 gallons of oil waste to non-detectable levels (Table 1).

Table 1. TREATMENT OF CONTAMINATED OIL, BUTTE, MONTANA

Contaminants	Concentration in	Concent Treated R		
CDD/CDF	Untreated Oil (ppb)	<u>70°C, 15 min.</u>	100°C, 30 min.	*MDC
TCDD (2,3,7,8-)	28.2	-	-	0.65
TCDD (total)	422	-	-	0.37
PeCDD	822	-	-	0.71
HxCDD	2982	-	-	2.13
TCDF (2,3,7,8-)	23.1	12.1	-	0.28
TCDF (total)	147	33.3	-	0.35
PeCDF	504	-	-	0.36
HxCDF	3918	4.91	-	0.76
HDCDF	5404	5.84	-	-1.06
OCDF	6230	-	-	2.62

*Minimum detectable concentration in parts per billion.

In May 1987, the KPEG was used at the request of U.S. EPA Region 7 to destroy TCDD in 20 gallons of 2,4-D/2,4,5-T formulation stored in a 55-gallon drum at an abandoned pesticide formulation facility in Omaha, Nebraska.

On January 22, 1987, documentation was provided to U. S. EPA's Director, Office of Emergency and Remedial Response, recommending the "Establishment of KPEG as the Best Developed Alternative Technology (BDAT) for Four RCRA Hazardous Waste Streams: PCBs and Ethylene Dibromide; Pentachlorophenol-oil and Spent Solvents Contaminated with Dioxins and Furans" (11). This recommendation was approved in 1987 by the Office of Emergency and Remedial Response in its Superfund cleanup efforts. Future efforts are directed at decontamination of soils, sediments, and sludges.

KPEG TREATMENT OF PCB-CONTAMINATED SOIL

In July 1987, a small KPEG reactor was transported to Moreau, New York, at the request of U.S. EPA Region 2, and used successfully to treat approximately 400 lbs. of PCB-contaminated soil.

The purpose of conducting the demonstration at Moreau was two fold: 1) to confirm that the KPEG reaction is effective in a 40 gallon reactor in the dechlorination of PCBs in soil to acceptable levels (< 2 ppm) and to gather data that will be used to design the larger 2 cubic yard reactor which will be jointly tested by U.S. EPA and the U.S. Navy in Guam. The results from the Moreau field tests (Table 2) clearly demonstrated that PCBs in soil ranging from 138 to 7012 ppm can be dechlorinated by KPEG to less than 10 ppm.

In November 1987, a new improved 400 gallon Littleford mixer was purchased, modified as a KPEG reactor, and will be field tested on 30 tons of soil on the U.S. Navy's Public Work Center in Guam. The PCB concentration in this contaminated soil range from 2500-4500 ppm. Field tests with the new reactor will commence on March 28 and will be completed by May 15, 1988.

Soil samples have been received from the Guam site, treated with KPEG and analyzed to establish treatment conditions to lower PCBs to less than 2 ppm. The laboratory testing and analysis for the Guam site follows.

GUAM PCB-CONTAMINATED SOIL TREATMENT AND REAGENT RECOVERY

The APEG treatment of PCB-contaminated soil is a rather straightforward process. It consists essentially of placing the contaminated soil into a reactor followed by a 50% by weight portion of the KPEG reagent. After loading, stirring and heating is commenced. Low speed stirring is required for intimate contact of reagent and contaminated soil. Heating causes two major effects, the first being distillation of water from the reaction mixture and secondly, to increase reaction rates. Typically, the vat temperature of the reactor remains near 105-110°C until the majority of water is distilled off (30-45 minutes) after which the reactor temperature slowly rises to ca 135-150°C. The total time for a typical reaction is from 5-6 hours.

After the required elapsed time, any condensate is removed and extracted for residual PCBs. The flask containing the treated soil/reagent mixture is

Run #1		Run #2		Run #3		Run #4	
Reaction time (hours)	PCB ⁿ , concentration (ppm)	Reaction time (hours)	PCB concentration (ppm)	Reaction time (hours)	PCB concentration (ppm)	Reaction time (hours)	PCB concentration (ppm)
0	138	0	756	0	7012	0	680
1.25	0.22	0.25	50.6	1	228	1	19.7
		4	1.46	3.25	23	3.25	6.5
				6.25	9.6	7	0,91

TABLE 2. TEST RESULTS FROM MOREAU FIELD DEMONSTRATION OF KPEG PROCESS

cooled to $40-50^{\circ}$ C and filtered on a Buchner funnel. An additional 25-30 ml of water is slurried with the reactor contents to aid in filtration.

After filtration and partial drying to 10-20% moisture, samples of the treated soil are removed and extracted for PCE (Aroclor) determination.

Recovered reagent/water is saved for reuse on subsequent decontamination runs. In this case recovered reagent from 2-3 runs is pooled, an additional quantity of 60% KOH solution or KOH pellets are added, and the used reagent is added to said reactor containing the contaminated soil. The process is then continued.

PCB ANALYSIS OF TREATED SOIL

The soil coming from the reactor is extracted for residual PCB or Aroclor determination. This process is as follows: 10 gram aliquots of the soil are placed into 125 ml screw-top Erlenmeyer flasks to which is added 30-35 ml of hexane/acetone (1:10), this is placed on a gyrorotary mixer at 120-130 rpm for one hour. The extract is carefully decanted into a 250 ml separatory funnel through a small funnel loosly packed with glass wool. This extraction is repeated twice again using hexane/acetone 1:1 and 10:1. All extracts are combined in said separatory funnel and the extracts are washed three times with 50 ml of water. The washed remaining hexane extract is placed into a KD apparatus fitted with a 10 ml receiver and is concentrated to ca 2-5 ml. The equipment is internally washed with hexane ca 2-4 ml and then the receiver is removed, filled to the 10 cc level and agitated. Approximately 2-3 ml of this sample is removed, placed into a 3.5 ml septa sealed glass sample container, and subjected to gas chromatographic analysis, either to an electron capture detector (EDC) or mass spectrometer (MS).

ANALYTICAL PROCEDURES

Generally, the in-house analytical procedure snalyzed for residual Aroclor(s) via capillary GC-ECD. In this system a 30 meter 0.32 mm I.D. DB-5 column, using an SGE cold on-column injector and a electron capture detector with Nitrogen make-up gas is employed for routine PCB analysis. However, for the Guam PCB/KPEG process, a HP GC-MSD with related data system for the analytical work has been utilized. In this case, the GC is equipped with a split/ splitless injector set to the splitless mode. The pumping requirements of the MSD require either use of a narrow bore capillary column (0.22 mm I.D.), or a jet seperator for use with packed columns. The narrow bore DB-5 column was used in this work.

The MSD is set to acquire data from M/Z 250-500 over the 16 to 32 minute range. The temperature program used for the GC is 40°C for 5 minutes ramp to 180°C at 25°C per minute, hold 2.5 minutes then ramp to 280°C at 5°C per minute, and hold 10 minutes. The total time per run is approximately 42 minutes. This method permits us to resolve the Aroclor mixture and is reliable for as low as 10 ppm of the Aroclor mixture.

For the analytical requirements to be used for the Guam PCB detoxification utilizing APEG, we have been requested to use the Dry Color Manufacturers Association (DCMA) PCB mixture. This mixture contains mono-thru-deca chlorebiphenyls, Any residual PCB peaks will be quantitated by comparison to this mixture. For example, were a hexachlorobiphenyl to remain after soil treatment, it would be quantified by comparison to the DCMA hexachlorobiphenyl. The maximum residual PCB levels which are permissible in this work are to be 2 ppm per resolvable PCB component. Therefore, all PCB peaks detected after treatment must be below 2 ppm (as shown in Figures 1.2.3).

CONCLUSION

As shown, the KPEG reagent has demonstrated its capability to reduce PCDDs and PCDFs to non-detectable levels in a variety of matrices. Further, the reagent can be used to reduce PCB levels from the thousands of ppm occurring from Aroclors 1248, 1254, 1260 and 1262 to levels below 2 ppm within a reasonable time frame. This demonstrates the use of KPEG systems applicability to these pollutants in a variety of matricies.

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Figure 1

UPPER: Aroclor 1260 extracted from Guam soil.

LOWER: Guam soil after treatment.



- Figure 2
- UPPER: Aroclor 1260 at 10 ppm.
- LOWER: Guam soil after treatment.



- Figure 3
- UPPER: Guam soil after treatment.
 DcmA
 LOWER: -CDMA PCB mixture
 (left to right = tetra, penta, hexa at 10 ppm
 and hepta, octa, nona and deca chlorobiphenyl at 5 ppm.)

IN-SITU BIODEGRADATION OF ORGANIC POLLUTANTS IN GROUNDWATER

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In Situ Biodegradation of Organic Pollutants in Ground Water

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Ground waters associated with hazardous wastes and wood preservation sites are often contaminated with the same chemicals found in surface soils. Depending on the hydrogeological characteristics of the site, <u>in situ</u> biorestoration technology may be applicable for remediation. <u>In situ</u> biorestoration involves stimulation of the indigenous microorganisms with limiting nutrients and oxygen to aerobically degrade both soluble and nonaqueous phase organic contaminants. <u>In situ</u> procedures will be illustrated with field experiments.

Subsurface Bioremediation of Creosote Contaminated Sites

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Introduction

Remediation of contaminated subsurface materials by in situ biorestoration involves stimulation of the indigenous subsurface microflora to degrade the contaminants (Thomas et al., 1987). The microorganisms are stimulated by the injection of inorganic nutrients and an appropriate electron acceptor into the subsurface. The process is generally used to remediate the dissolved (contaminant plume) and sorbed (bound to subsurface materials by physical/chemical mechanisms) phases of contaminants such as liquid fuels and creosote, rather than the concentrated source of the contamination. In addition, the more homogeneous the contamination, the more amenable it is to treatment. The inherent problem in treating contaminant mixtures is ensuring the biodegradation of all the contaminants.

The majority of subsurface materials which have been remediated by in situ biorestoration have been contaminated with liquid petroleum fuels. However, contaminants associated with wood preservation are known to be biodegradable. Compounds other than liquid fuels which have been treated in situ include mineral oil hydrocarbons, waste solvents, and alkanes (Thomas et al., 1987) Compounds such as methylene chloride, n-butanol, dimethylaniline, acetone, ethylene glycol, isopropanol, tetrahydrofuran, and chloroform have been treated by withdrawal and treatment above ground, followed by recharge of the reactant mixture which has been amended with nutrients and oxygen.

Inoculation of the subsurface with microorganisms to enhance biodegradation is an undemonstrated technique, although the addition of "magic bugs" has been an intergal part of many remedial programs. Basically, the role of added microorganisms in such in situ biorestoration schemes has never been distinguished from that of the indigenous microflora. In order for the added microorganisms to be effective, they must be transported to the zone of contamination, colonize the subsurface solids, and grow (Thomas et al., 1987). The rate and extent of microbial transport will depend on the characteristics of the aquifer and bacteria. The most important aquifer characteristic which will affect microbial transport is permeability. Cells which are bigger than the average pore size of the matrix will not be transported. In addition, the cells may be removed from the injection fluid by sorption to clay and organic matter or by the formation of aggregates which are too big to pass through the pore spaces. Provided that the microorganisms are transported, the cells must colonize the subsurface matrix and become established as part of the subsurface ecosystem. In addition, the introduced cells must retain their special metabolic capabilities for degrading the contaminants and compete with the indigenous microflora for nutrients, which may become limiting during the biorestoration process.

There are basically five steps in the in situ biorestoration process: 1) determining the presence of contaminant-degrading microorganisms, 2) conducting a thorough site investigation, 3) recovering free product, when applicable, 4) conducting laboratory studies to determine the nutrient requirements of the indigenous microflora and the compatibility of the nutrients with the subsurface material, and 5) designing and implementing the system.

Determining the presence of contaminant-degrading microorganisms

In general, subsurface microorganisms are present, metabolically active, and can degrade a variety of chemicals of environmental concern (Thomas et al., 1987). Compounds such as acetone, ethanol, isopropanol, tert-butanol, methanol, benzene, and many alkylbenzenes,

chlorinated benzenes, chlorinated phenols, and polycyclic aromatics have been shown to biodegrade in samples of subsurface material. Ring compounds more complex than pyrene frequently found in creosote are very difficult to degrade microbiologically (Heitkamp et al., 1988a; Heitkamp et al, 1988b).

Although microorganisms have been detected in many samples of subsurface materials (Beeman and Suflita, 1987; Federle et al., 1986; Ghiorse and Balkwill, 1983; Webster et al., 1985; Wilson and McNabb, 1983) it can not be assumed that they are ubiquitous. Analysis of some samples has indicated minimal or no microbial activity. Ground water collected from one contaminated site contained less than 10 cells/ml and the microflora in these samples did not respond to the addition of oxygen and nutrients (Brubaker and Crockett, 1986). Other instances of little or no microbial activity in the subsurface have been reported. The glucose amendment in unsaturated material from a creosote waste pit was not mineralized whereas the glucose in saturated material from the same borehole, and in less contaminated and pristine unsaturated and saturated materials from the same site, was mineralized (Lee, 1986). The inhibition was thought to be the result of high concentrations of creosote sludge in the unsaturated zone in the waste pit.

On the other hand, microorganisms may be present in the subsurface but unable to degrade the contaminants. For instance, a glucose amendment was mineralized in subsurface material from both clean and contaminated areas at a site contaminated with aviation fuel; however, biodegradation of benzene and toluene, compounds found at high concentrations in aviation fuel, was observed in samples from the contaminated area only (Lee, 1986). Biodegradation of benzene and toluene in the contaminated but not the uncontaminated samples suggests that a period of adaptation, or exposure of the microorganisms to the contaminants, may be required before significant biodegradation will occur. Adaptation may result from an increase in the population of contaminant degraders, a mutation which codes for new metabolic capabilities.

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induction or derepression of enzymes responsible for degradation of specific contaminants (Aelion et al., 1987), or may be related to the concentration of the contaminant of interest, and nutrients (Swindoll et al., 1988).

Provided that contaminant-degrading microorganims are present and metabolically active in the subsurface, the major factor limiting biodegradation in the subsurface is an adequate supply of nutrients and an electron acceptor (generally oxygen; nitrate has been used on a limited basis). As a result of the highly carbonaceous nature of most contaminants, any natural biodegradation which occurs after a spill will quickly exhaust the ambient levels of nitrogen, phosphorus, and electron acceptors. Further biodegradation will depend on the rate of recharge of electron acceptors from mixing at the edge of the plume (Wilson et al., 1985) and the turnover of nitrogen, phosphorus, and trace elements required for microbial metabolism. Additions of oxygen and inorganic nutrients to laboratory samples and in the field have been shown to increase the rate of biodegradation of many ground water contaminants (Lee and Ward, 1984; Raymond et al., 1986; Swindoll et al., 1988).

The presence of contaminant-degrading microorganisms in the subsurface is determined in laboratory studies. Samples of core material are collected and used to determine the biodegradation potential of selected contaminants in biotransformation and/or mineralization experiments. Biotransformation experiments are conducted by adding contaminated core material to incubation vessels and measuring the disappearance (biotransformation) of the contaminants using gas chromatography. Mineralization experiments are conducted by adding contaminated by adding contaminated core material to incubation vessels, amending the contents with a ¹⁴C-labeled contaminant of interest, and measuring the amount of ¹⁴CO₂ evolved (mineralization) from the labeled compound using liquid scintillation counting. There are pros and cons for both methods. In general, biotransformation experiments may be better predictors of biodegradation potential than mineralization experiments because the compound may be converted into cell mass and/or

other products, and not evolved initially as CO₂. Experiments which measure mineralization would not indicate the conversion of the compound into products other than CO₂. Biotransformation experiments can be used to determine the fate of several compounds simultaneously, provided that the contaminants of interest are physically and chemically similar, and extracted and chromatographed using the same methods. However, diverse contaminant mixtures may require extensive analytical workups which are time-consuming and costly. In addition, the disappearance of the parent compound measured by gas chromatography simply indicates that the parent compound has been altered, and is not a good indicator of whether or not the contaminant has been metabolized to a less hazardous or innocuous compound. To determine the presence of potentially hazardous intermediates or products in biodegradation pathways, the gas chromatography analysis should be coupled with mass spectrometry . A gas chromatography-mass spectrometry workup on a mixture of compounds will be expensive.

Mineralization experiments provide direct and positive proof of the ultimate destruction of the contaminant in a single analysis: the conversion of the compound to CO₂. Mineralization experiments can be expensive to conduct because of the cost of the ¹⁴C-labeled material and equipment required for scintillation counting. However, mineralization experiments may be cheaper than an extensive gas chromatography-mass spectrometry workup for a contaminant mixture. In contrast to biotransformation experiments in which several structurally similar contaminants can be investigated simultaneously, mineralization of only one compound at a time can be determined. However, mineralization is advantageous because the high sensitivity of the assay and the time required for analysis is short.

Site investigation

The subsurface formation must be permeable enough to allow the transport of an electron acceptor, usually oxygen, and inorganic nutrients to the microflora in the zone of contamination. The rate and extent of transport of the nutrient solution will depend on the hydraulic conductivity (K) of the formation under investigation. Formations with K values of 10⁻⁴ cm/sec or greater are usually considered good candidates for in situ biorestoration (Thomas et al., 1987). Therefore, the first step in the feasibility study of an affected area is to determine the K value at the site. The K value, expressed in distance per time, indicates the rate at which a fluid moves through a medium, and is a function of the fluid and the type of medium. The hydraulic conductivity, which in the past has been referred to as the permeability, can be determined using a variety of methods which include 1) slug tests, 2) pump tests, 3) variable head tests, and 4) tracer tests. The type of test used depends on the formation and the amount of money available to conduct the test. The geology at the site can be determined from U.S. Geological Survey maps or from other sources available on the geology of the site. The composition of the aquifer must be determined before a method for obtaining the K value is chosen. The slug test is used in relatively nonpermeable formations whereas the variable head. pump tests and tracer tests can be used in basically any formation. Whereas the slug and variable head tests are cheap to conduct, the pump and tracer tests are more expensive. However, the pump and tracer tests provide information over a large volume of the aquifer while the slug and variable head tests provide measurements within a short radius of the well.

Knowledge of the K values at multiple locations is desirable because of the spacial heterogeneity of the subsurface (Thomas et al., 1987). In addition to longitudinal heterogeneities, vertical variability in K also needs to be considered to accurately predict spreading (dispersion) of contaminants and nutrients (Moltz et al., 1986). Verticle variability

can be accounted for by determining K values using multi-level sampling wells. Tracer tests have been developed which measure vertically variable K values. Knowledge of aquifer heterogeneities is important because transport of nutrients and the electron acceptor into zones of low permeability can be limited or prevented. Partial transport of the nutrient solution into low permeability zones could result in incomplete remediation.

Other aquifer characteristics that will be important in implementing in situ biorestoration will be the direction and rate of ground water flow, depth to the water table and zone of contamination, and the specific yield of the aquifer. In addition, the dynamic characteristics of the aquifer, such as hydraulic connections to other aquifers, recharge and discharge, and water table fluctuations should be considered.

Recovery of Free Product

When applicable, as in the case of a liquid fuel spill or liquid creosote deposits, free product should be removed before installation of an in situ biorestoration system. Implementation of the bioremediation system before free product recovery would be wasteful because of the enormous quantities of nutrients which would be required to biodegrade the contaminants (Huriburt, 1987). In addition, the high concentrations of the contaminants may be toxic to the subsurface microflora. The amount of product that can be recovered will depend on the characteristics of the formation. Highly permeable formations with little associated organic carbon should yield the highest recoveries. Free product can be recovered using a variety of well systems, all of which take advantage of the fact that hydrocarbons are relatively insoluble in and less dense than water. Basically, the hydrocarbons float in a cone of depression which is created by pumping at a lower depth (Knox et al., 1986). Materials heavior than water such as creosote are more difficult to recover since they tend to sink to the bottom of the solurated zone.

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Nutrient Requirements and Compatibility

Contamination of the subsurface with highly carbonaceous wastes results in ratios of carbon to nitrogen, phosphorus, and trace elements which are too wide to allow significant microbial metabolism. In addition, the concentration of dissolved oxygen, the preferred electron acceptor in biodegradation of most contaminants, is usually too low. Laboratory experiments should be conducted to determine the inorganic nutrient requirements of the subsurface microflora. These tests should be conducted using samples of subsurface solids rather than the ground water. Studies have indicated that the microflora in well water may not be representative of that associated with subsurface solids (Thomas et al., 1987). In addition, an analysis of the ground water for inorganic nutrients will not provide information concerning the nutrient requirements can be determined by incubating contaminated subsurface material with different combinations of inorganic nutrients.

Even in the presence of sufficient inorganic nutrients, biodegradation will be limited without sufficient levels of an electron acceptor. The preferred electron acceptor for the majority of contaminants will be oxygen. Although many petroleum-derived compounds can be biodegraded anaerobically, the rates are faster under aerobic conditions. The rate-limiting step in aerobic biodegradation of the contaminants will be the rate of transfer of oxygen to the microorganisms. Optimum biodegradation would therefore be achieved by transporting high concentrations of dissolved oxygen to the subsurface microflora as fast as possible.

Oxygen can be added to the subsurface by air sparging, as pure oxygen, or as hydrogen peroxide (H_2O_2). Depending on the temperature of the ground water, air sparging and the addition of pure oxygen can achieve dissolved oxygen concentrations of about 9 and 40 mg/L, respectively. Hydrogen peroxide, which is completely miscible in water, can achieve much higher concentrations of dissolved oxygen. However, H_2O_2 can be toxic to microorganisms at

concentrations as low as 200 ppm. Before addition of H_2O_2 to the subsurface, laboratory experiments should be conducted to determine the tolerance level of the subsurface microflora to the peroxide. In the field, the initial concentration of H_2O_2 injected is usually low (1 ppm), and then increased gradually to concentrations as high as 500 ppm. Between step increases in peroxide concentration, microbial numbers in ground water should be monitored to assess potential toxic effects.

Although oxygen is the accepted electron acceptor for hydrocarbon biodegradation, the use of nitrate has been investigated. Remediation of one gasoline spill was accomplished by adding nitrate to aerated water, which was then injected into an aquifer to treat a hydrocarbon spill (Batterman, 1983). The nitrate was added to serve as an electron acceptor after the oxygen was depleted. Of the 22.5 tons of hydrocarbon retained in the subsurface, approximately 7.5 tons was removed within 120 days. Nitrate was added to an experimental field plot in Ontario, Canada, which was artificially contaminated with a gasoline plume (Berry-Spark and Barker, 1987). Data obtained from an extensive monitoring system at the site indicated that degradation of toluene, ethylbenzene, and m-xylene was greater in the nitrate-amended plume than in a control plume which did not receive nitrate.

After the inorganic nutrient requirements of the subsurface microflora are determined, experiments must be conducted to determine the compatibility of these nutrients with the subsurface material. Analyses of both the ground water and subsurface materials are required to determine the potential for precipitation and/or complexation of added nutrients with reactive components in the formation. In formations with high levels of ferrous iron (Fe⁺²), the addition of oxygen can precipitate the iron out of solution as ferric iron (Fe⁺³), which can plug the formation. In addition to decreases in permeability, the formation of iron oxide consumes oxygen and renders it unavailable for microbial metabolism. Hydrogen peroxide may also be consumed by reactive materials in the subsurface and rendered unavailable. The dissociation of
H_2O_2 may be affected by reactive species in the subsurface material (Raymond et al., 1986). Catalysts of peroxide decomposition which may be present in subsurface materials include iron, copper, manganese, and chromium. Rapid dissociation may form oxygen bubbles which plug the formation. To control the rate of decomposition, orthophosphate salts may be added to complex the catalysts. In contrast, H_2O_2 may not decompose fast enough in sand and gravel aquifers with low organic carbon and no natural catalysts. Catalytic metals, ususally chelated, or enzymes such as the oxidases and peroxidase, may be added to enhance H_2O_2 decomposition. Depending on the results of these nutrient compatibility experiments, the concentrations of the electron acceptor and/or nutrients should be adjusted accordingly or the injection solution amended to prevent nutrient precipitation and/or decomposition problems.

System Design and Implementation

After the laboratory experiments and site investigation have been completed, the system for injection of the electron acceptor and inorganic nutrients is implemented. The type of well system used will depend on the characteristics of the site under investigation. Basically, the oxygen source and inorganic nutrients are injected into the subsurface through injection wells or infiltration galleries while recovery wells are pumped (Figures 1 and 2). Infiltration galleries allow infiltration of the injection solution through the unsaturated as well as the saturated zone. Some operational designs are closed loop in which the water is recycled, thus recycling any unused nutrients and avoiding disposal of potentially hazardous ground water. The inorganic nutrients are usually added first, followed by the oxygen source. Simultaneous addition of the two may cause microbial growth close to the point of injection and consequent plugging of the aquifer. The inorganic nutrients may be added in batch or continuously. Continuous addition

of the oxygen source may be advantageous because low dissolved oxygen levels are likely to be the rate-limiting step in hydrocarbon degradation. Heterogeneities in the aquifer, such as impermeable lenses and variable hydraulic conductivities, will hinder the distribution of nutrients and oxygen. Once the system is operating, careful monitoring of hydrocarbon concentrations, dissolved oxygen and nutrient levels, and microbial numbers is necessary.

Mathematical models can be used to design the injection and production system and predict the progress of the bioremediation (Thomas et al., 1987). Models which predict bioremedial progress require 1) a rate coefficient for biodegradation 2) a term which describes the abiotic processes which affect contaminant and nutrient transport, and 3) a procedure which combines the effect of the biotic and abiotic processes and simulates the remedial progress. The injection and production system can be designed by modeling the site-specific hydraulic parameters. Most models which are developed to describe contaminant transport and fate in ground water are based on the advection-dispersion equation which describes the control of contaminant transport by ground water flow (advection) and contaminant spreading (dispersion). Models have been developed that predict transport and biodegradation of contaminants in the saturated zone under oxygen-limited conditions. BIOPLUME and BIOPLUME II are models which have been developed to predict transport and biodegradation of ground water contaminants (Borden and Bedient, 1986; Borden et al., 1986; Rifai et al., 1988).

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FIGURE 1. Typical schematic for aerobic subsurface biorestoration. (after Raymond <u>et al.</u>, 1978)



FIGURE 2. Use of infiltration gallery for recirculation of water and nutrients in *in situ* biorestoration.

ONSITE BIOREMEDIATION OF WOOD PRESERVING

CONTAMINANTS IN SOILS

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Abstract

Bioremediation of soils at wood preserving sites involves the use of naturally occurring microorganisms to destroy specific chemicals, usually pentachlorophenol (PCP) and polycyclic aromatic hydrocarbons (PAH), associated with the soil at the site. Several wood preserving locations on the Superfund List of NPL sites have been identified for possible bioremediation. Types of biological treatment systems currently considered for remediation of contaminated soils at wood preserving sites include: (1) Land Treatment as defined in the Resource Conservation and Recovery Act (RCRA), (2) In Situ Treatment, and (3) Bioreactor Treatment. This paper addresses the goals of onsite bioremediation of soils and current treatment systems for using bioremediation at wood preserving sites, summarizes the status of selected sites currently considering or using bioremediation, and identifies important questions concerning bioremediation that should be part of any evaluation strategy when considering the potential application of bioremediation for wood preservative contaminated soils.

Introduction

The Superfund Amendments and Reauthorization Act of 1986 (SARA) produced major changes in the original Superfund law, including strongly favoring permanent remedies which implement risk reduction (control) technologies that mitigate or eliminate risks at Superfund sites. SARA established requirements for the development and use of cost-effective treatment technologies, in accordance with the requirements of the National Contingency Plan (NCP), that offer permanent protection of human health and the environment. The use of naturally occurring microorganisms to accomplish destruction and detoxification of hazardous constituents for the protection of health and the environment is consistent with the philosophical thrust of SARA and is the goal of onsite bioremediation of wood preserving contaminated soils (Figure 1).

Bioremediation of soils at wood preserving sites involves the use of naturally occurring microorganisms to destroy specific chemicals, usually pentachlorophenol (PCP) and polycyclic aromatic hydrocarbons (PAH), associated with the soil at the site. The subject of bioremediation of contaminated soils, including applications and limitation of the technology, has been addressed at



Figure 1. The Goals of Onsite Bioremediation of Contaminted Soils.

several recent scientific meetings and conferences (1,2,3,4). Three aspects that are important for considering in order to accomplish bioremediation of contaminated soils include: (1) waste and site characterization, (2) microbial activity and growth of soil microorganisms, and (3) treatment system design and management. Wood preserving waste characterization, including physical and chemical properties and specific chemical constituents, have been addressed by Dr. McGinnis at this Forum and by others (5,6), and therefore is not addressed in detail in this paper. Factors affecting activity and growth of aerobic heterotrophic microorganisms in soil involved in hydrocarbon and chlorinated hydrocarbon biodegradation have been addressed in detail in other publications (5,6,7) and are only considered in this paper where specific applications are discussed. This paper addresses treatment systems that are currently being used and that are designed based on knowledge of waste characteristics, microbial ecology, and soil processes.

Treatment Systems

Three categories of treatment systems currently considered for bioremediation of soils contaminated with wood preserving wastes include: (1) Prepared bed systems, i.e. land treatment as characterized in the Resource Conservation and Recovery Act (RCRA), (2) In-Situ systems, and (3) Bioreactor systems. Information requirements applicable for all of these treatment systems include: (1) identification of factors influencing and limiting biodegradation, (2) biodegradation rate evaluation and stimulation, (3) extent of degradation and formation of intermediate products, and (4) monitoring of treatment performance (8,9,10). The information requirements are used for each treatment system to meet the goals of on-site bioremediation of contaminated soils illustrated in Figure 1.

Prepared bed and land treatment systems involve the controlled application and intimate mixing of contaminated materials into the upper zone of soil in a prepared bed, in order to degrade and transform organic contaminants and to immobilize inorganic contaminants, thus, leading to an environmentally acceptable assimilation of such contaminants (9). Degradation and detoxification represent primary mechanisms for the assimilation of the organic contaminants. Land treatment technology is designed to accomplish simultaneous treatment and ultimate disposal. Based upon waste and soil characteristics, specific management techniques are frequently used to optimize the activity of naturally occurring indigenous microorganisms to accomplishment treatment. Specific management the incorporation of materials into the soil using techniques include mass loadings and frequencies of application that are not inhibitory to soil microbial processes, addition of the nutrients nitrogen and phosphorus, tilling to facilitate the transport of oxygen through the soil, and pH adjustment. Additional management techniques for stimulating microbial destruction of organic recalcitrant chemicals include irrigation and the addition of easily degradable carbon substrates, for example, fresh manure or green vegetation.

Information concerning mechanisms involved in land treatment and demonstrated results in laboratory and field scale tests provide a significant information base concerning the applications of this biotreatment technology (9,10,11,12,13,14,15,16,17,18). Additional information concerning the functions and processes operating within a land treatment unit treating hazardous chemicals are provided in the Permit Guidance Manual on Hazardous Waste Land Treatment Demonstrations (9).

In situ biotreatment systems involve the controlled manipulation and management of soil microbial processes and of soil physical and chemical processes that affect natural soil microbial processes in order to achieve degradation and detoxification of wood preserving organic waste constituents. In situ treatment may be used for: (1) surficial soils generally less than three feet below the surface of the soil, and (2) subsurface (vadose zone) soils that lie between surficial soils and the groundwater table. In situ treatment systems are designed to meet the goals of onsite bioremediation (Figure 1) without physically removing or isolating the contaminated soil from the contiguous environment. Successful application of in situ treatment requires information and understanding of site, soil, and waste interactions. Specific waste, site and soil characteristics that are important for determining the potential success for in situ treatment are summarized in Tables 1 and 2, and discussed in detail elsewhere (6).

Management techniques for in situ bioremediation involve the manipulation of influencing biological activity factors including nutrients, oxygen, moisture, and pH (20). Addition of amendments, including microorganism inoculations, to surficial soils generally has fewer restrictions with regard to mass transfer than amendments applied to deeper soils. Manipulation of factors influencing microbial activity, rather than addition of specially adapted microorganisms is preferred because the addition of specially prepared microorganisms to soil environments has significant current technical, ecnomic, and regulatory constraints (21,22).

Above ground bioreactors also can be used to treat contaminated soil at wood preserving sites. Bioreactors are generally based on design fundamentals taken from chemical and environmental engineering reactors that have been designed to effect specific chemical and biological reactions. Therefore, bioreactors can be categorized as: (1) suspended growth slurry reactors, (2) fixed film reactors, (3) completely stirred tank reactors (CSTR), and (4) plug flow (PF) reactors. Suspended growth reactors contain high concentrations of bacteria that move with the liquid and that use the surrounding aqueous medium as a support medium for growth, while fixed film reactors utilize inert supports for the attachment of bacteria that treat water that "passes over" the retained bacteria (23). Completely mixed reactors have a uniform composition throughout the reactor so that the treated material leaving the reactor has the same composition as the material in the reactor; plug flow reactors resemble "pipe flow" and have a gradient in the composition of treated material within the reactor from the "input" side of the pipe to the "output" side. Bioreactors are generally built above-ground in vessels where contaminated materials, amendment addition, and environmental conditions can be controlled to accomplish the biological destruction and detoxification of organic chemicals associated with contaminated soils that would be added to the reactor as the waste material for treatment.

Table 1.Site and Soil Characteristics Identified as Important in In SituTreatment (Reference 6)

Site location/topography and slope Soil type and extent Soil profile properties boundary characteristics depth texture* amount and type of coarse fragments structure* color degree of mottling bulk density* clay content type of clay cation exchange capacity* organic matter content* pH* Ēh* aeration status* Hydraulic properties and conditions soil water characteristic curve field capacity/permanent wilting point water holding capacity* permeability* (under saturated and a range of unsaturated conditions) infiltration rates* depth to groundwater,* including seasonal variations flooding frequency runoff potential* Geological and hydrogeological factors subsurface geological features groundwater flow patterns and characteristics Meteorological and climatological data wind velocity and direction temperature precipitation water budget

*Factors that may be managed to enhance soil treatment

Table 2.Soil-based waste characterization (Reference 6)

Chemical class	
acid	
base	
polar neutral	
nonpolar neutral	
inorganic	
Soil sorption parameters	
Freundlich sorption constants (K, N)	
sorption based on organic carbon content (K _m)	
octanol/water partition coefficient (K_{ow})	
Soil degradation parameters	
half-life (t ₁₀)	
rate-constant (first order)	
relative biodegradability	
Chemical properties	
molecular weight	
melting point	
specific gravity	
structure	
water solubility	
Volatilization parameters	
air/water partition coefficient (K_w)	
vapor pressure	
Henry's law constant $(1/K_{w})$	
sorption based on organic carbon content (K_{oc})	
water solubility	
Chemical reactivity	
oxidation	
reduction	
hydrolosis	
precipitation	
polymerization	
Soil contamination parameters	
concentration in soil	
depth of contamination	
	-

Current Sites Using Bioremediation

Several wood preserving sites currently are being considered for application of bioremediation technology. These sites are identified in Table 3. Table 4 contains a summary that includes the following information for each site where information was obtained: Site name, location and EPA Region, contact person, target clean-up levels, the organization conducting the remediation, and information concerning the treatment systems and the status of the site remediation.

Combinations and modifications of the treatment systems discussed above have been used at wood preserving sites to optimize treatment and to achieve the goals of onsite bioremediation identified previously. For example, a combination of prepared bed land treatment and bioreactor systems is currently employed at the Burlington Northern site in Minnesota. Because the natural soils are fine sands with high permeability, pilot studies and the full scale implementation include a liner (100 mil HDPE membrane) and leachate collection system (two feet wide collection drains at 100 feet centers) to prevent possible leachate breakthrough. Land treatment of contaminated soils was optimized based on treatability studies using naturally occurring organisms present at the site that indicated that the following operating and design criteria were important: (1) soil moisture should be maintained near field capacity, (2) soil pH be maintained between 6 and 7, (3) soil carbon:nitrogen ratios should be maintained between 25:1 and 50:1. (4) fertilizer applications should be completed in small frequent doses, (5) waste reapplication should occur after initial soil concentration have been effectively degraded, and (6) waste reapplication rates of 2 to 3 pounds of benzene extractable hydrocarbons per cubic foot of soil per three-degradation months could be effectively degraded. Animal manure was also applied at a loading rate of two percent of soil (dry weight basis) to provide nutrients and organic matter, which provides organic matter to enhance retention of organic chemicals in the sandy soils to allow biodegradation to occur. Bioremediation at this site is approximately 50 percent complete and is presently considered a success by personnel involved in the remediation (24).

Another combination of treatment systems is being proposed at the Baxter/Union Pacific Tie Treating Plant site in Laramie, Wyoming. Field scale studies involving a combination of in situ and bioreactor treatment have recently begun. The approach involves saturating the unsaturated zone by raising the water table, pumping solutions through the saturated area, treating the solution in above ground reactors, followed by subsurface injection of the treated solution into the soil. Similar to the above example, the process uses naturally occurring microorganisms indigenous to the site. Additional information concerning specific case histories of bioremediation of hazardous waste sites was presented by Ross et al (25).

An important aspect of onsite bioremediation of wood preserving

contaminated soil is the lack of agreement on target clean-up levels or criteria. As indicated for the sites summarized in Table 4, target clean-up levels vary from site to site, with some clean-up levels not determined at this time. Criteria that are being considered in formulating target clean-up levels include risk assessment, land ban targets, and negotiation based on site-specific constraints.

Table 3.	Wood	preserving si	tes where	bioremediation	has	been	proposed	for
	soil or	lagoon sedim	ents				-	

	Site Name State	(Region)	Proposed Remediation
1	L.A. Clark and Sons	VA (3)	Bioremediate
2	Brown Wood Preserving	FL (4)	Bioremediate
3	Burlington Northern (Brainard)	MN (5)	Landfarm
4	North Cavalcade Street	TX (6)	Bioremediate
5	United Creosoting Company	TX (6)	In Situ remediation
6	Baxter/Union Pacific	WY (8)	Bioreclamation
7	Burlington Northern (Somers)	MT(8)	Landfarm
8	Libby (Champion International)	MT (8)	In Situ Bioremediation and Landfarm
9	Koppers, Co.	CA (9)	Bioremediate
10	J.H. Baxter	CA (9)	Bioremediate

Status of wood preserving sites where bioremediation has been proposed Table 4.

L.A. Clark & Sons Spotsylvania City, VA (Fredricksberg, VA)

Region III

Harry Harbold, U.S	S. EPA, (215)597-4914
Contaminants:	Creosote
Media:	Ground water, surface water, and soil/lagoon sediments contaminated
Record of Decision:	Soil/lagoon sediments 3/88; ground water 1989
Proposed Remediation:	Bioremediation and flush soil/lagoon sediments

Summary:

- 40 acre site, with contamination to water table (12 feet)
- Pumpout free creosote, flush soil, follow with in situ bioremediation
- No treatability studies now -- in the future -
- Consent decree: -
 - Cleanup levels based on risk: 10³ ground water, with soil cleanup levels back-Cleanup levels based on fisk: 10 ground water, with soil cleanup levels back-calculated using a model Estimated 5 years to clean up site at estimated cost of \$24 million After 3 years the company can recommend an alternative method; this is a private party cleanup by the company (Union Pacific and L.A. Clark & Sons) -
 - -_

Approach in the future:	Laboratory treatability studies, followed by field study; in situ approach no dig up and removal/transport
Firms Involved:	MOTEC may be involved in EPA SITE program for biological treatment of sludges in the lagoon using a batch biological treatment system (in tank treatment - bioreactor).

Table 4. Continued

Brown Wood Preserving Live Oak, FL

Region IV

John Vargo (Project Manager), U.S. EPA, (404)347-2643

Contaminants:	Creosote
Media:	Soil and lagoon sediments contaminated
Record of Decision:	4/88
Proposed	

Remediation: Bioremediation of soil

Summary:

- Dismantled the facility and removed contaminated soils and sludges with "creosote" concentrations greater than 1,000 ppm to Alabama waste disposal site (this included all sludges); 160,000 tons of soils/sludges; site size is about 40 acres
- Bioremediate residual contaminated soil with "creosote" concentration less than 1,000 ppm using landfarming technology, about 6,000 cu. yd soil
- Short-term treatability studies were conducted in laboratory columns; based on results a field-scale engineering treatment scheme was developed based on landfarming technology:
 - (1) Prepare a 4-acre "treatment" site with clay liner (1 ft. to 3 ft. thick), site with 1% grade, above ground irrigation;
 - (2) Will use 6-inch lifts to treat soil; anticipate needing only two 6-inch lifts to treat the 6,000 cu. yd. soil;
 - (3) Target for cleanup is 100 ppm or less "creosote" which is based on risk assessment (dermal contact); a 2-year time limit has been given for treating all contaminated soil to 100 ppm target;
 - (4) After treatment is complete, site will be covered with soil and seeded;
 - Note: Natural microorganisms in the soil that are involved in PAH degradation will be "concentrated" in "tanks" and sprayed on the treatment area during a "one-time" event at the beginning of the treatment to "seed" the site with microorganisms; microorganisms have already been identified

This is a private party cleanup; Brown foundation is paying RETEC to clean up the site; State of Florida has been actively involved;

Bioremediation technology appears to be appropriate and successful for this site. Use of "natural" microorganisms, i.e., no seeding with "special" organisms or "genetically engineered" organisms, is preferred.

Firms Involved: Remediation Technology (RETEC)

Table 4.Continued

Burlington Northern (BN) (Brainard Site) Brainard/Baxter, MN

Region V

Lonna Beilke (MPCA Project Manager), (612)296-7745 Ginny Yingling (MPCA On-Site Inspector), (621)296-7824 Amy Blumberg, U.S. EPA, (312)353-9306

Contaminants: Creosote

Media: Ground water, soil/lagoon sediments contaminated

Remedial Investigation/ Feasibility Study: Completed 1984

Proposed

Remediation: Landfarm soil/lagoon sediments 1986; Pumpout ground water

Summary:

- Ron Linkenheil (Remediation Technology) and Ginny Yingling (MPCA) Lonna Beilke (MPCA)
- About 50% completed -- field bioremediation; completed second full season
- Remediation on top of original impoundment; lined impoundment site; not a clean closure (not dig up and remove)
 - Contamination to depth of 25 feet
 - Tracking PAHs
 - Plan to place cap on top
 - 95% sand site -- need liner to collect possible leachate
 - No biological treatment of contaminated ground water discharge to Mississippi River (NPDES) based on comparison with paper industry
 - Storage pile next to pond while site remediation system was under construction
 - Center pivot irrigation
 - Source removal -
 - Visual criteria -- dig up soil with free oil and black color
 Clean up goals -- less contamination than material left behind 1,000 mg/Kg total PAH - end (negotiated) 20,000 mg/Kg total PAH - start

Operation: Long time clean up because only use 3 acres, with repeated applications to keep material "on site"

Firms Involved: Remediation Technology (RETEC)

Table 4.Continued

North Cavalcade Street Houston, TX

Region VI

Louis Rogers (State Lead Site) Texas Water Commission (513) 463-8171

Contaminants:	Creosote
Media:	Soil or lagoon sediments, ground water
Remedial Investigation/ Feasibility Study:	Complete
Record of Decision:	Signed in 1988 and specified biological treatment as the preferred alternative. In situ remediation is desired if feasible.

Summary:

- The site is underlain by sand and clay lenses. If in situ treatment is not feasible, then "dry phase" land treatment will be evaluated; if this approach is not chosen, slurry reactors (above ground vessels) will be evaluated. The major concern with land treatment is the potential for air emmissions. Control of air emissions associated with "dry phase" treatment may be achieved; however, through use of an air inflatable dome.
- The amount of contaminated soil to be bioremediated is 130,000 cubic yards. The initial concentration of creosote was greater that 200 ppm total PAH. The target level for cleanup of the soil is 100 ppm total PAH. The time frame for cleanup is two years (1992).

Table 4. Continued

United Creosoting Company Conroe, TX

Region VI

Louis Rogers (State Lead Site), Texas Water Commission (512) 463-8171

Contaminants:	Creosote, pentachlorophenol, dioxins		
Media:	Soil or lagoon sediments, ground water		
Remedial Investigation/ Feasibility Study:	Completed		
Record of Decision:	Interim ROD signed in 1988		

Summary:

- Treatability studies are presently being conducted for "dry phase" land treatment. A high density polyethylene (HDPE) liner will be used. Contaminated soil will be brought into the lined area and managed at optimum moisture. Soil will be aerated daily. Animal manure is added to augment biological degradation of PAH compounds. Microorganisms from the site have been cultured and added to the contaminated soil once at the initiation of the study. The soil will be remediated in batches on the several-acre site. No specific time frame for cleanup has been identified.
- Results to data are vey promising based on laboratory scale (one square meter) plots prepared in the field at the site. If the "dry phase" treatment is not successful, the second alternative is to use critical phase solvent extraction.
- Amount of contaminated soils is approximately 70,000 cubic yards. The target level for cleanup of the soil is approximately 100 mg/kg total PAH, based on the recommendation of the Center for Disease Control (CDC). This soil level is based on avoiding chronic health impacts through ingestion.

Firms Involved: Roy F. Weston, Houston, Texas

Table 4. Continued

Baxter/Union Pacific Tie Treating Laramie, WY

Region VIII

Terry Anderson, U.S. EPA Section Chief, (303)293-1790 Felix Flechas, Project Manager, (303)293-1669

Contaminants:	Creosote, some PCP
Media:	Ground water, surface water, and soil/lagoon sediments contaminated
Record of Decision:	09/86; remedial action in progress
Proposed Remediation:	Oil recovery, soil washing, bioremediation
Implemented Remediation:	Bench scale lab testing; field scale now

Summary:

- Felix Flechas (EPA)
- RCRA 3008H Corrective Action Site; on NPL
- 200-300 acre contamination associated with tie treating plant
- 20 feet depth contamination to bedrock contaminated
- Actions Included:
 - (1) Remove pond sludges;
 - (2) Move river;
 - (3) Place slurry wall 70 feet deep around site;
 - (4) Drain lines inside and outside of wall to maintain hydraulic gradient into contaminated area (inside lower than outside)
- Laboratory Studies: (Phase 1, short-term evaluation) -- done Determine potential for bioremediation using "on-site" microorganisms; enhancement studies also conducted; mineralization of organics investigated; additional laboratory studies were requested to provide more information
- Field Scale Studies: (Phase 2, recently begun) -- ongoing In situ bioremediation: pump solution through aquifer, treat in reactor above ground, subsurface inject into soil with organisms; isolated cells using sheet piling for hydraulic control -- raise water level for "treatment" to make unsaturated zone saturated by passage of solution from surface through subsurface; will use site kinetics for extrapolation of time required for concentration reduction; have not determined the target level(s) for cleanup; waiting for RCRA numbers to be promulgated

- Surface bioremediation in soil in old wood preserving pond (lagoon bottom soils). Pond . bottom is clay soil that is contaminated; 20% oil in soil
- Cleanup of lagoon pond bottom -- activities -- Land Treatment Mode _
 - Lab studies by ECOVA, Seattle, of pond bottom, land treatment mode for treatment (1) "in-place"; microorganism counts, PAH and PCP chemistry included in laboratory studies
 - Pilot studies -- next; add manure and nutrients to pond bottom; monitor air quality (2) including dust which occurs with tilling operations; sprinkler irrigation on 7 plots;

 - maintain soils at 80% field capacity; Can use on-site soil to mix with pond bottom soil Treatment will be "layer-by-layer"; uppermost layer will be treated, then removed, and next (top) layer will be treated, until, layer-by-layer, soil is treated down to (3) (4) water table

Ecova, CH₂M Hill **Firms Involved:**

Table 4. Continued

Burlington Northern (BN) Somers, MT

Region VIII

Stephanie Wallace, U.S. EPA, (406)449-5414

Contaminants:	Creosote, metals
Media:	Ground water, surface water, soil/lagoon sediments contaminated
Remedial Investigation/ Feasibility Study:	Complete, under EPA review
Proposed Remediation:	Remove and landfarm soil/galoon sediments, removal of standing water and sludges in 1985

Summary:

- Possibility -- landfarm materials at Paradise, MT, 60 miles away
- Land Treatment Demonstration completed at Paradise, MT RCRA Part B - not permitted yet; don't know if facility at Paradise will be permitted to accept additional Somers waste
 - Two problems:
 - Permit for Paradise (1)
 - (2)Volumes of wastes for treatment limited by additional capacity at Paradise waste pile and land treatment unit
 - (a)
 - if 10⁶ cleanup of soil (0.9 mg/Kg) is used 75,000 cu. yd. if 10⁵ cleanup of soil (9.2 mg/Kg) is used much less soil (b)
- Distance from source area to water table varies from 15 feet depth in one source area to iust below surface in another. Located on north shore of Flathead Lake
- Paradise is a RCRA Corrective Action site; Somers will be a joint RCRA/CERCLA Consent Decree
- Land Treatment is considered good for creosote treatment since metals are not expected to be a problem; however, air emissions may be a problem under Land Ban. Total capacity of waste pile is 18,500 yd³.

Table 4.Continued

Libby Groundwater (Champion International) Libby, MT

Region VIII

Ken Wallace, U.S. EPA, (406)449-5414

Contaminants:	Creosote, dioxin, PCP, metals, volatiles
Media:	Ground water and soil/lagoon sediments contaminated
Feasibilty Study completed:	11/88
Record of	00/86 Altemate water supply
Decision:	12/88 - Clean up
Proposed	•
Remediation:	In situ bioremediation and land farming

Summary:

- Bench Scale Studies:
 - Soil cores studies conducted by Dr. Gary McGinnis, Mississippi State University, to determine organic degradation rates, mobility, etc.
- Land Treatment Demonstration Unit:
 - Approximately 7/88 to 10/88 to obtain field data on degradation rates and migration potential. Carried out RCRA land treatment guidance.
- Ground Water Biorestoration Study:
 - Approximately 7/87 to 9/88, to obtian field data on potential of in situ bioremediation of upper aquifer. Oxygen injected constantly, and nutrients by batch, in four ground water ports. Monitoring wells down gradient sampled frequently for bacteria counts, contaminant concentrations, DO, nitrogen content, etc.

Record of Decision: Signed December, 1988

- Soils: First Step Excavate small source areas and concentrate in large waste pit source area. In situ initial treatment using enhanced biomass (imported bacteria, sugar, fertilizer, product) to effect a rapid and significant reduction in creosote and PCP concentrations. Second Step - Remove lift of treated soil from waste pit area and place in lined treatment unit. Continue treatment until cleanup goals are achieved. = 30,000 yd³.
- Upper Aquifer:Site wide in situ biorestoration program to be implemented. Oxygen and nutrients will be injected at selected wells to increase natural bacterial populations in the ground water and increase the degradation of organic compounds. Closed injection/extraction system will be installed around the waste pit area to remove free product from saturated zone and physically treat the highest concentration area.

- Lower Aquifer: Traditional product extraction methods considered ineffective for site. ROD calls for a lab and field study of innovative clean up technologies, including in situ biorestoration in conjuction with primary and secondary oil recovery, to assess whether aquifer can be practicably remediated.

Clean up goals:	Water - MCLs and 10 ^{-s} risk
• •	Soils - Land Disposal BDAT (K001) and 10 ⁻⁵ risk

Firms Involved: Woodward-Clyde Consultants, MOTEC

Table 4.Continued

Koppers Co., Inc., Oroville Plant Oroville, CA

Region IX

John Kemmerer, U.S. EPA, (415)974-7112

Contaminants:	Creosote, PCP, CCA
Media:	Ground water, surface water, soil/onsite canal sediments, dioxin/furans contaminated
Record of	
Decision:	Scheduled for September, 1989
Remedial options under	
consideration:	Pump and treat ground water; wash, biroremediate, or incinerate soil/lagoon sediments

Summary:

;

- Fire in 1987 resulted in dioxin formation, dust problems, temporary cap on top

- A landfarm treatability study was conducted while State of CA was lead; PCP leached through soil; bioremediation options would now need liners

Firms Involved: Keystone Environmental Resources

20

Table 4. Continued

J.H. Baxter Weed, CA

Region IX

Carolyn Thompson, U.S. EPA, (415)974-8257 Leo Levinson, U.S. EPA, (415)974-7101

Contaminants:	Creosote, PCP, metals (AS,CR)
Media:	Ground water, surface water, soils/lagoon sediments contaminated
Record of Decision:	Scheduled for October, 1989
Proposed Remediation:	Bioremediate, incincerate, or fix soil/lagoon sludges

Summary:

- Approximately 20 acres of contaminated soil, with depth of contamination approximately 20-30 feet;
- Dr. Gary McGinnis, Mississippi Forest Products Laboratory, has conducted laboratory treatability studies on biodegradation of creosote constituents. The effect of the metals present in contaminated soil on biodegradation is of concern. Steel tanks have been constructed on site that contain soil to simulate soil treatment under field conditions. The steel tanks have been constructed to prevent migration to ground water; units began operation on October 1, 1988.
- Issues concerning this site:
 - (1) Cleanup targets based on risk assessment must be determined; use land ban targets?
 - (2) Metals migration in contaminated soils, especially arsenic and chromium; fixation in soils
- Possibilities for remediation:
 - (1) Remove free creosote;
 - (2) Excavate some soil and remediate using land treatment technology;
 - (3) In situ treat residual soil

Bioremediation Technology - Preliminary Screening Information

When considering the potential application of onsite bioremediation of wood preserving contaminated soils, there are several issues that should be considered as part of any preliminary evaluation. Bioremediation is often limited by factors that include: (1) distribution of the waste limits access to the waste; (2) supply of nutrient(s) required for metabolism; (3) toxicity of waste due to concentration of waste constituents; (4) formation and accumulation of toxic byproducts; (5) inadequate population(s) of requisite microorganisms; (6) non-competitiveness or non-survivability of inoculated cultures; (7) absence of capable microorganisms, (8) inadequate management of the system. Prior to the application of any onsite bioremediation system for the treatment of wood preserving contaminated soil , the factors identified above should be addressed for each potential treatment system.

For each treatment system considered, the following information should be obtained with regard to the site-specific application of the technology: (1) type(s) of information needed, (2) evaluation of commercial claims, (3) potential problems and limitations, (4) data gaps, and (5) current research focus and research results that may be useful in designing treatability studies or in field-scale implementation of the treatment system. The importance of conducting degradation and detoxification treatability experiments with appropriate controls, and conducting a site characterization to identify environmental and ecological factors that will affect the process under field conditions cannot be overemphasized. Evaluation of commercial claims should involve side-by-side comparisons in time using appropriate and statistically rigorous experiments including controls that duplicate the commercial process but exclude the commercial product.

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EXISTING DATA ON WOOD PRESERVING WASTE INCINERATION

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PRESENTATION BY DONALD A. OBERACKER - RISK REDUCTION ENGINEERING LABORATORY

PART I: EXISTING DATA ON WOOD PRESERVING WASTE INCINERATION

PART II: EXAMPLES OF MOBILE/TRANSPORTABLE HAZARDOUS WASTE INCINERATION TECHNOLOGIES FOR FIELD SITE CLEANUP OPERATIONS

PART I

EXISTING DATA ON WOOD PRESERVING WASTE INCINERATION

OCTOBER, 1988

ΒY

DONALD A. OBERACKER TECHNICAL SUPPORT SPECIALIST U.S. ENVIRONMENTAL PROTECTION AGENCY OFFICE OF RESEARCH AND DEVELOPMENT RISK REDUCTION ENGINEERING LABORATORY
INTRODUCTION

The purpose of this paper is to provide a brief perspective on how incineration might be considered a solution for the cleanup of abandoned or problem land sites where wastes from wood preserving industries have caused pollution problems.

As an initial outlook position, this author believes that both the contaminated soils which may include low ppm to percentage amounts of tetra- or pentachlorophenols and other compounds such as benzene, toluene, and various polynuclear aromatics as well as actual pockets of the waste sludges or liquids or their leachates can readily be treated by high temperature incineration processes to result in cleaned or "sterilized" soil residues. The cleaned material which will be in the form of dried soil/ash can then be set back in place if desired, thus restoring the site for normal commercial or even residential" purposes. Of course, some may consider the post-treated soils more as "fill material", and this is very true since incineration will strip out all organics, leaving the soil void of natural nutrients necessary to grow grass or plants and therefore a laye¹ of good top soil would be needed on top as a finishing step.

Procedurally, one would probably only consider incineration for cases where relative open fields or easily accessable or excavatable soil and/or contaminated groundwaters are involved. Obviously, soils underneath substantial buildings which are inaccessable would not be considered for incineration.

In addition, an initial study must be made to determine whether the excavated material would be best treated on site by a mobile on transportable incinerator brought to the site or if the soil should be hauled to a fixed or stationary commercial incinerator facility. For the purposes of this presentation at least, it will be assumed that hauling to a distant stationary incinerator is not feasible, due to economics or availability consideration AVAILABLE PERFORMANCE DATA

The first four overheads or figures show the summary results of four specific incineration tests that EPA has performed on the types of chemical contaminants in

treated wood, or wastes from the wood treating industry. It should be noted that this presentation covers only the creosote or tetra-pentachlorophenol types of wood preservatives and does not cover the newer metal types of materials.

Figures 1, 2, and 3 show the overal2 characteristics of the wastes incinerated and the performance results which generally demonstrate the effectiveness of incineration. Figures 1-3 are considered "pilot-scale" operations, while figure 4 reports on a fieldscale operation. All of these tests were made on relatively small fixed incinerators, however it would be expected that larger units or mobile and transportable units would be able to accomplish similar results since the primary need is for adequate handling, combustion temperatures, and residence times, etc. Figure 4 stands out as an exception in terms of performance, however, showing that some amounts of dioxins and furans can be emitted from the incinerator stack. It is believed that this condition of incompletely destroyed pollutants was the result of the lower (below 1800F) temperature conditions that were prevelant in this particular incinerator. Operating this unit at conditions closer to that which EPA used in its pilot tests most likely would have resulted in much cleaner, probably undetectable levels of these pollutants.

CONCLUSIONS

In conclusion, while there is only a limited amount of data on file as shown to indicate the incinerability of wood preserving wastes of the organic type, this author believes that there is sufficient grounds to seriously consider incineration as a treatment method for such sites. The chemical compounds themselves, being more easily destroyed than other commonly incinerated compounds such as carbon tetrachloride, PCBs, and chlorobenzenes, etc., are considered by many to be "easily incinerated".

Nevertheless, any plan or activity which incorporates incineration at any specific site should probably include, as a beginning, test or trial burns of the specific waste and incinerator combination up front to prove its viability.

INCINERATION TRIAL BURN BY EPA'S INDUSTRIAL ENVIRONMENTAL

RESEARCH LABORATORY (IERL), CINCINNATI - 1983

- TEST FACILITY: LOS ALAMOS NATIONAL LABORATORY, (DOD) CONTROLLED AIR INCINERATOR BY ENVIRONMENTAL CONTROL PRODUCTS, MODEL 500-T (NOMINAL 500 LBS./HR.), WITH MINOR MODIFICATIONS TO FACTORY UNIT.
- WASTE DESCRIPTION: KOREAN WAR-VINTAGE ARMY AMMUNITION BOXES TREATED WITH PENTACHOROPHENOL (PCP), CRUSHED
- WASTE ANALYSIS: CHLORINE CONTENT - 0.07 PERCENT BY WEIGHT PCP CONTENT - 0.103 to 0.106 PERCENT BY WEIGHT PINE WOOD WITH 7960 (ACTUAL) AND 9066 (DRY) BTU/LB
- RESULTS: DRE FOR PCP WAS GREATER THAN 99.99% NO TCDD IN STACK EMISSIONS (DET. LIMIT 1 PPB) NO TCDF IN STACK EMISSIONS (DET. LIMIT 5 PPB) ASH - NOT SAMPLED AND ANALYZED
- WASTE FEED RATES: 60 100 LBS./HR.
- INCINERATION CONDITIONS: 1800 F FOR A GAS RESIDENCE TIME OF 1.5 SECONDS

RREL DATA ON INCINERATING WOOD PRESERVING WASTES

- TEST FACILITY: EPA COMBUSTION RESEARCH FACILITY ROTARY KILN SUMMER OF 1987
- WASTE DESCRIPTION: KOO1-PENTACHLOROPHENOL (PCP) TYPE

ALLIED CHEMICAL'S AMERCIAN WOOD DIVISION OF POWER TIMBER COMPANY, RICHTON, MISSISSIPPI

BOTTOM SEDIMENT/SLUDGE FROM WASTEWATER TREATMENT CONTAINING PCP (INCLUDING PENTA- AND TETRACHLORO-PHENOLS, VOLATILE ORGANIC SOLVENTS, E.G. BENZENE, TOLUENE, AND POLYNUCLEAR AROMATIC (PNA) PARTS OF CREOSOTE)

ANALYSIS:	SOIL	40%
	WATER	30%
	WOOD CHIPS	10%
	ACTIVE ORGANICS	20%
		100%

ASH CONTENT HEATING VALUE PCP 12-51% 3800-8300 BTU/LB. 970-3800 PPM

RESULTS: NON-DETECTABLE FOR ALL PRIORITY RCRA VOLATILE AND SEMI-VOLATILE COMPOUNDS IN ASH AND IN SCRUBBER WATER (INCLUDING DIOXINS/FURANS)

STACK TESTING RESULTS NOT AVAILABLE AT THIS TIME

RREL DATA ON INCINERATIN WOOD PRESERVING WASTES (CONTINUED) SUMMER OF 1987

- TEST FACILITY: JOHN ZINK COMPANY ROTARY KILN
- WASTE DESCRIPTION: KOO1-C (CREOSOTE TYPE)
 - ALLIED CHEMICAL'S BIRMINGHAM, ALABAMA PLANT, BOTTOM SEDMIENT SLUDGE FROM TREATMENT OF WASTEWATERS FROM PROCESSES USING CREOSOTE, THIS MATERIAL OBTAINED FROM THE PEARL RIVER WOOD PRESERVING CORPORATION, PICAYUNE, MISSISSIPPI

SOIL	30%
WATER	20%
WOOD CHIPS	10%
NAPTHALENE	4%
PHENANTHRENE	3.5%
FLUORANTHENE	2.5%
OTHER ACTIVE ORGANICS	30%
	100%
	SOIL WATER WOOD CHIPS NAPTHALENE PHENANTHRENE FLUORANTHENE OTHER ACTIVE ORGANICS

ASH CONTENT
HEATING VALUE
VOLATILE MATTER

12.51% 10,000-11,000 BTU/LB. 57-81%

RESULTS: NON-DETECTABLE FOR ALL PRIORITY RCRA VOLATILE AND SEMI-VOLATILE COMPOUNDS IN ASH AND IN SCRUBBER WATER (INCLUDING DIOXINS/FURANS)

STACK TESTING RESULTS NOT AVAILABLE AT THIS TIME

INCINERATION DATA BY EPA'S TIER 4 NATIONAL DIOXIN STUDY 1986-7

TEST FACILITY: INDUSTRIAL CONTROLED AIR INCINERATOR WITH WASTE HEAT BOILER

- WASTE DESCRIPTION: PAINT FILTERS AND DRY PAINT, PAINT SLUDGE, AND WOOD/PLASTIC SCRAP MATERIAL FROM MANUFACTURE OF PCP-TREATED WOOD/PVC PLASTIC COATED STORM WINDOWS, WOOD FRAMING TREATED WITH 0.1 LB/FT³ PCP
- RESULTS: FOR AN AVERAGE FEED RATE OF 2390 LB/HR TO THE INCINERATOR;

TOTAL PCDD EMISSIONS:1370 MICROGRAMS/HOUR (STACK)2,3,7,88.62TOTAL PCDF EMISSIONS:4600

ASH ANALYSES:

TOTAL PCDD:	1 to 302.6 PPB
2,3,7,8	ND to 0.2 "
TOTAL PCDF:	0.07 to 17.7 PPB

INCINERATOR TEMPERATURES:

PRIMARY CHAMBER: 1100 to 1800 F (AVG. 1392 F) SECONDARY CHAMBER: 940 to 1820 F (AVG. 1480 F)

FACILITY: ANDERSEN WINDOW COMPANY

PART II

EXAMPLES OF MOBILE/TRANSPORTABLE HAZARDOUS WASTE

INCINERATION TECHNOLOGIES

FOR

FIELD SITE CLEANUP OPERATIONS

OCTOBER, 1988

BY

DONALD A. OBERACKER TECHNICAL SUPPORT SPECIALIST U.S. ENVIRONMENTAL PROTECTION AGENCY OFFICE OF RESEARCH AND DEVELOPMENT RISK REDUCTION ENGINEERING LABORATORY

INTRODUCTION

In this PART II of my presentation, I have focused on the technologies or actual available incinerator hardware in the commercial sector which could very likely be employed in the cleanup of contaminated wood preserving waste sites. An underlying assumption is that most or all of these sites are of a sufficiently small size or tonnage in total to be handled by mobile or transportable incinerators situated on the site itself. However, I do recommend that in all cases, the logistics, legality, and economics of transporting the waste or contaminated soils themselves to ancexisting, stationary incinerator (if available) be considerd.

Figures 5 through 17 presented as overhead projections are intended to carry one common theme, namely that the mobile/transportable incinerator industry is very much "existing and available". Virtually all of the firms involved got their concept or start in this business by following the impetus of EPA's mobile incinerator, and/or EPA's engineering study which examined the design feasiblity of larger transportable units. The figures provide the reader an idea of the relative size and in some cases the past accomplishments of the unit in terms of cleaning up sites of various types of pollution.

CONCLUSIONS

As the presentation indicated, there are a host of available mobile/transportable incineration firms with a variety of hardware available on the market. This paper makes no attempt to steer or recommend the potential user towards any one particular firm or brand of incinerator, but rather simply presents the names and characteristics of some of the units which are readily known. The list of manufacturers is not necessarily complete -- that is, there may well be a few additional firms who have entered this marketing area.

It is recommended that any particular site cleanup action should probably begin by testing the commercial market for interest in the project as a first step, then advancing toward normal request for proposals and bids as the project moves along.

DEFINITIONS

- MOBILE: LARGELY MOUNTED ON SEMI-TRAILERS AND MEETING LEGAL OVER-THE-ROAD SPECIFICATIONS, MINIMUM ON-SITE CONSTRUCTION
- TRANSPORTABLE: MOSTLY INVOLVING FIELD ERECTION/ASSEMBLY OF TRUCK-TRANSPORTED COMPONENTS, SIGNIFICANT BUT TEMPORARY EQUIPMENT FOUNDATIONS, BUT DISASSEMBLED UPON JOB COMPLETION

EPA'S MOBILE INCINERATION SYSTEM WHICH INSPIRED THE DEVELOPMENT AND GROWTH OF SIMILAR PORTABLE/TRANSPORTABLE FIELD SITE INCINERATION SYSTEMS IN THE COMMERCIAL SECTOR

OVERALL CHARACTERISTICS:

- DEVELOPED BY ORD DURING APPROXIMATELY 1970-1982
- INITIAL PERFORMANCE TESTS AT EPA-EDISON, NEW JERSEY ON PCBs AND RCRA WASTES
- SET UP IN REGION VII IN DECEMBER, 1984 FOR DENNY FARM DIOXIN CONTAMINATED SOILS, DEBRIS, AND LIQUIDS
- ACCOMPLISHMENTS TO DATE:

OVER 3 MILLION POUNDS OF SOLIDS OVER 200,000 POUNDS OF LIQUIDS AVERAGE THROUGHPUT: 3,000 POUNDS PER HOUR 70 PERCENT ON-LINE TIME

- SYSTEM DESCRIPTION:

NOMINAL 12 MILLION BTU/HR. TOTAL ROTARY KILN 52 IN. ID x 16 FT. LONG AFTERBURNER 52 IN. ID x 36 FT. LONG HOT CYCLONE PARTICLE SEPARATOR WET ELECTROSTATIC PRECIPITATOR AIR OR OXYGEN PLUS FUEL OIL FIRED SHREDDER

- CURRENT STATUS:

TO BE DETERMINED

LARGER, TRANSPORTABLE CONCEPT:

EPA ORD SPONSORED INITIAL FEASIBILITY/DESIGN STUDIES IN EARLY 1980's

STATIONARY PILOT-SCALE FACILITIES FOR DIAGNOSTIC TEST-BURNS OF SAMPLE QUANTITIES OF VARIOUS CONTAMINATED SOILS AND OTHER WASTES

> EPA'S COMBUSTION RESEARCH FACILITY JEFFERSON, ARKANSAS (ORD-CINCINNATI)

- ROTARY KILN PLUS AFTERBURNER, 3 MILLION BTU/HR. (4 FT. DIAMETER x 6 FT. LONG)
- LIQUID INJECTION UNIT PLUS AFTERBURNER, 3 MILLION BTU/HR.
- PERMITS: RCRA, PCB, DIOXIN
- SAMPLE SIZE: 4 TO 10 DRUMS MIN.

JOHN ZINK COMPANY, TULSA, OKLAHOMA

- ROTARY KILN PLUS AFTERBURNER, 3-5 MILLION BTU/HR. (3 FT. DIAMETER x 15 FT. LONG)
- LIOUID INJECTION UNIT PLUS AFTERBURNER, 3 MILLION BTU/HR
- PERMITS: RCRA (NO PCB)
- SAMPLE SIZE: 10 TO 20 DRUMS MIN.

EXAMPLES OF COMMERCIAL FIRMS ACTIVE IN FIELD SITE CLEANUP VIA INCINERATION WITH MOBILE/TRANSPORTABLE SYSTEMS

- ENSCO CORPORATION LITTLE ROCK AND ELDORADO, ARKANSAS
- WESTON SERVICES INCORPORATED WEST CHESTER, PENNSYLVANIA
- INTERATIONAL TECHNOLOGY (IT) CORPORATION KNOXVILLE, TENNESSEE
- VESTA TECHNOLOGY LTD. FT. LAUDERDALE, FLORIDA (THERMALL, INC.)
- THERMAL INCORPORATED PEAPACK NEW JERSEY
- WILLIAMS ENVIRONMENTAL SERVICES INCORPORATED STONE MOUNTAIN, GEORGIA
- ROLLINS ENVIRONMENTAL SERVICES INCORPORATED ATLANTA, GEORGIA; WILMINGTON, DELAWARE; DEER PARK, TEXAS
- ENVIRITE FIELD SERVICES INCORPORATED ATLANTA, GEORGIA AND PLYMOUTH MEETING, PENNSYLVANIA
- CHEMICAL WASTE MANAGEMENT INCORPORATED CHICAGO, ILLINOIS

ENSCO CORPORATION MOBILE OR TRANSPORTABLE INCINERATORS

- SIX (6) MOBILE UNITS (3 IN FINAL CONSTRUCTION)
- SMALLER UNITS ARE 5-6 TONS/HR (4 UNITS EXIST)
- LARGER UNITS ARE TRANSPORTABLE, 20 TONS/HR (CONSTRUCTION SCHEDULED FOR COMPLETION IN FALL, 1988)
- UNITS HAVE BEEN IN USE AT TAMPA, EL DORADO, GULFPORT, AND SMITHPORT (CANADA)
- COMPOUNDS TREATED:

PCBs, DIOXINS, HERBICIDE ORANGE, OTHER RCRA CHEMICALS IN CONTAMINATED SOILS

- SITE INVOLVEMENT:

TAMPA, FLORIDA CHICAGO EL DORADO, ARKANSAS (SUPPLEMENTS MAIN PCB UNIT) GULFPORT, MISSISSIPPI TEXAS SMITHVILLE (CANADA) RICHMOND, VIRGINIA

WESTON SERVICES, INCORPORATED TRANSPORTABLE INCINERATOR

- ROTARY KILN 7 FT. DIAMETER x 25 FT. LONG
- AFTERBURNER 8 FT. DIAMETER x 33 FT. HEIGHT
- FABRIC FILTER APCD SYSTEM
- PACKED TOWER HCL CONTROL UNIT
- DESIGN CAPACITY 6 TONS/HOUR ON CONTAMINATED SOIL & DEBRIS
- USED AT: BEARDSTOWN, ILLINOIS (5,000-10,000 TONS)
- COMPOUNDS TREATED: PCBs (UP TO 1% OR 10,000 PPM IN SOIL)

INTERNATIONAL TECHNOLOGY (IT) TRANSPORTABLE INCINERATOR

- ONE (1) UNIT EXISTS, HAS BEEN USED IN COMPLETING THE INCINERATION OF THE CORNHUSKER SITE (40,000 TONS OF TNT & DINITROTOLUENE & TRINITROBENZENE CONTAMINATED SOILS - EXPLOSIVES)
- TWO (2) MORE UNITS UNDER CONSTRUCTION (1989) INTENDED FOR MOTCO (TEXAS) SITE WITH PCB AND STYRENE TAR CONTAMINATION
- ROTARY KILN IS 6-1/2 FT. DIAMETER x 45 FT. LONG, COUNTERCURRENT
- AFTERBURNER IS VERTICAL, 1200 C
- TOTAL HEAT CAPACITY IS 56 MILLION BTU/HR (EITHER KILN PLUS AB OR AFTERBURNER ALONE)
- SOIL THROUGHPUT CAPACITY NOMINALLY 20 TONS PER HOUR, OVER 15 DEMONSTRATED

VESTA TECHNOLOGY LTD. MOBILE INCINERATORS (USING THERMALL TECHNOLOGY)

- TWO (2) UNITS EXIST, "VESTA 80" and "VESTA 100"
- MODEL 80 IS A 8 MILLION BTU UNIT WITH A 5.03 FT. DIAMETER BY 16 FT. LONG KILN AND A 5.03 FT. DIAMETER BY 20 FT. LONG AFTERBURNER
- MODEL 100 IS A 10 MILLION BTU/HR. UNIT WITH A 4.33 FT. DIAMETER BY 25 FT. LONG KILN AND A 5.33 FT. DIAMETER BY 30 FT. LONG AFTERBURNER
- CAPACITIES CLAIMED:

MODEL 80: 1000-2000 POUNDS PER HOUR OF SOILS MODEL 100: 3000-5000 POUNDS PER HOUR OF SOILS

- SITES TREATED:

REGION I IN ASHLAND, MASSACHUSETTS, 1200-1600 TONS OF NITROBENZENE CONTAMINATED SLUDGES, PART OF A 35 ACRE SITE WITH CONCENTRATIONS UP TO 9100 PPM, COMPLETED

REGION IV IN ABERDEEN, NORTH CAROLINA, 5000 POUNDS OF HAZARDOUS WASTE CONSISTING OF SOILS CONTAMINATED WITH CARBON TETRACHLORIDE AND PESTICIDES, COMPLETED

- FUTURE SITES:

DELRAY BEACH, FLORIDA, 3000 CU. YDS. OF PESTICIDE CONTAMINATED SOIL

CHEHALIS, WASHINGTON, PENTACHLOROPHENOL AND DIESEL FUEL CONTAMINATED DEBRIS

THERMALL INCORPORATED (ALSO SEPARATELY SUPPLIED VESTA'S UNITS)

- UNITS IN DESIGN PHASE:

A 4 TON/HR UNIT WITH 25 MILLION BTU/HR CAPACITY USING A 6.5 FT. DIAMETER KILN BY 28 FT. LONG

A 6 TON/HR UNIT WITH 35 MILLION BTU/HR CAPACITY USING A 8 FT. DIAMETER KILN BY 35 FT. LONG

- AVAILABILITY:

4 TON/HR UNIT EXPECTED TO BE COMPLETE IN SPRING OF 1989

6 TON/HR UNIT IN DESIGN PHASE, COMPLETION NOT SPECIFIED

ROLLINS ENVIRONMENTAL COMPANY'S ROTARY RECTOR TRANSPORTABLE SYSTEM (FORMERLY "PEDCO/PEI FAST ROTARY REACTOR")

- 33.5 MILLION BTU/HR ROTARY KILN W/FLUIDIZED SAND, RECIRCULATING
- KILN IS 3.3 METERS (10.9 FT.) DIAMETER x 65 FT. LONG
- FORCAST CAPACITY 150 TONS/DAY OF 2500-3500 BTU/LB.
 MATERIALS (CLAIMED SELF-SUSTAINED COMBUSTION AT THAT BTU)
- FIELD-TRANSPORTABLE VERSION TO HAVE DRY SCRUBBING (NO WATER USE)
- CURRENT UNIT UNDER TEST IN DEER PARK, TEXAS
- SMALLER, PILOT UNIT TESTED 1986 IN STATIONARY MODE, USED A 2 FT. 4 IN. ID x 18 FT. LONG KILN/REACTOR
- DEVELOPED BY PEI OF CINCINNATI, OHIO COAL OFFICE, AND UNIVERSITY OF CINCINNATI
- TARGET BUSINESS:
 - INITIAL: LARGE SAMPLE TEST BURNS AT DEER PARK ON SUPERFUND SOILS, ETC.
 - LATER: TRANSPORT TO FIELD SUPERFUND SITES
- STATUS:

INSTALLED AND UNDERGOING HOT TESTING IN OCTOBER, 1988

STATIONARY TESTING WITH SOLID/LIQUID RCRA & PCB WASTES IN FALL, 1988 (DIOXIN PERMIT POSSIBLE)

PLANS TO CONVERT TO FIELD-TRANSPORTABLE UNIT USING DRY-SCRUBBER IN 1989

LOOKING FOR SITES TO APPLY

ENVIRITE FIELD SERVICES INCORPORATED TRANSPORTABLE INCINERATOR

- LARGE ROTARY KILN PLUS AFTERBURNER, RATED AT 82 MILLION BTU/HR WITH SOILS OF 1200 TO 2000 BTU/LB.
- SOILS THROUGHPUT CAPACITY 15 TONS/HR
- USES BAG HOUSE (FABRIC FILTER) PLUS WET SCRUBBER
- HAS INCINERATED CREOSOTE CONTAMINATED DREDGED LAGOON SLUDGES WHICH WERE STABILIZED WITH CEMENT KILN DUST FOR HANDLING (NO PCPs, ONLY PNAS) (THE PRENTISS, MISSISSIPPI SITE OF 7500-9500 TONS, NOT COMPLETED)

CHEMICAL WASTE MANAGEMENT'S TRANSPORTABLE ROTARY KILN: "PY-ROX" UNIT

IN CONSTRUCTION AT SAUGET, ILLINOIS (TWI FACILITY)

50 MILLLION BTU/HR.

CONSTRUCTION STARTED: 6/88 (PERMITTED TO BUILD BY IEPA) SCHEDULED TO OPERATE 3/89

OTHER UNITS AT:

KETTLEMAN HILLS, CALIFORNIA (PERMIT APPLIED FOR) MODEL CITY, NEW YORK (IN PERMITTING) MEMPHIS, TENNESSEE (PROPOSED)

ALL UNITS UTILIZE DRY SCRUBBER + FABRIC FILTER (BAG HOUSE)

CAPACITY CLAIMED: 30,000 TONS/YR.

REMAINING ISSUES AND RECOMMENDATIONS

ISSUES:

PERMITTING

TYPE AND CONCENTRATION OF ANY HEAVY TOXIC METALS

AFFORDABILITY OF INCINERATION (\$200 TO \$500 AND UP PER TON NET)

PRE-PROCESSING REQUIREMENTS (SHREDDING, MATERIALS HANDLING, SOLIDIFYING LAGOON LIQUIDS AND SOLIDS, ETC.)

RELEASE OF POLLUTANTS DURING EXCAVATION AND HANDLING

DELISTING AND DISPOSAL OF TREATED MATERIAL

RECOMMENDATIONS:

DESIRABILITY OF DIAGNOSTIC TEST BURNS AT PILOT SCALE

INCLUDE ALL REAL COST ITEMS (SAMPLING AND ANALYSIS, MONITORING, SITE CLEANUP AND CLOSURE, ETC.)

CONSIDER MULTIPLE BIDDERS AND TECHNOLOGIES

PUMP-AND-TREAT TECHNOLOGY

Dr. Joseph F. Keely, Portland, Oregon

* * * Preliminary Outline * * *

PUMP-AND-TREAT TECHNOLOGY

by

Joseph F. Keely, Ph.D., P.Hg., FAIC/CPC Ground-Water Quality Consultant

a presentation delivered to the

U.S. EPA FORUM ON REMEDIATION OF WOOD PRESERVING SITES U.S. EPA Region IX, San Francisco 24-25 October 1988

I. Introduction

- purpose (contaminant removal & plume isolation)
- traditional conceptual basis (how pump-and-treat works)
- state-of-the-science conceptual basis (how it doesn't work)

II. Design

- principal system components (wells, header system, etc.)
- drawdown cones vs. capture zones
- effects of partial penetration, streams, etc.
- contaminant transport data needs

III. Operation

- hydrodynamic effects, limitations (esp., velocity regions)
- chemical and biological effects, limitations
- continuous operation vs. pulsed pumping
- IV. Compliance and Performance Monitoring
 - hydrodynamic vs. chemical monitoring
 - hydrodynamic compliance monitoring strategies
 - performance evaluation strategies

PUMP AND TREAT TECHNOLOGY

Joseph F. Keely, Ph.D., P.Hg., FAIC/CPC Ground-Water Quality Consultant Suite 2002, Tanasbourne Mall 2700 NW 185th Avenue Portland,Oregon 97229

presented to

FORUM ON REMEDIATION OF WOOD PRESERVING SITES U.S. EPA Region IX San Francisco, CA 24 October 1988

FORUM ON REMEDIATION OF WOOD PRESERVING SITES

PUMP AND TREAT TECHNOLOGY

by

Joseph F. Keely, Ph.D., P.Hg., FAIC/CPC

Wellfield Hydrodynamics

Pumping and injection wellfields comprise an effective method of generating substantial changes in the direction and rate of ground-water flow. The principle involved is purely physical: lower the fluid pressure in the aquifer locally (by pumpage) and an immediate convergence of flow lines is centered on the source of the pressure reduction (the pumped well). Alternately, raise the fluid pressure in the aquifer locally (by injection) and an immediate divergence of flow lines is centered on the source of the injection well). Regionally, the flow system suffers a minor, localized disturbance. Locally, the flow system yields nearly radially to the well; not only does ground water flow to a pumping well from the [pre-operational] upgradient side of the well, but from the [pre-operational] downgradient side also. The distance downgradient from which a pumping well will be able to draw waters back to itself is defined as the *stagnation point* (Keely and Tsang, 1983).

1. Capture Zones

More precisely, the stagnation point of a single pumping well is located at that distance downgradient where the velocity of flow back to the well, caused by pumpage, is directly offset by the velocity of flow away from the well caused by the natural flow system. The stagnation point is the downgradient limit of the *capture zone* of a single pumping well; the lateral limits of the capture zone are found at a distance from the centerline (e.g., the line that bisects the well along the upgradient-downgradient axis) equal to the value obtained by multiplying the stagnation point distance by the mathematical constant pi. The capture zone is that portion of the aquifer that contains ground water that will be eventually *captured* and discharged by the pumping well. It does not include the entire zone of pressure influence (drawdown cone) generated by the pumping well, unless the natural flow system velocity is zero (Keely, 1984).

2. Rejection Zones

By reversing the frame of reference, it can be seen that a stagnation point forms upgradient of injection wells. The push of waters out of the well in the [pre-operational] upgradient direction is directly countered by the movement of the natural flow system in the [pre-operational] downgradient direction. The stagnation point that forms in this circumstance is at the upgradient limit of the *rejection zone*. The lateral limits of the rejection zone are, of course, found at a distance from the centerline equal to the value obtained by multiplying the stagnation point distance by the mathematical constant **pi**. The rejection zone is that portion of the aquifer which will eventually contain only injected water (the native water in the formation is displaced first), and which does not allow the entry of additional native waters. It does not include the entire zone of pressure influence (injection cone) generated by the injection well, unless the natural flow system velocity is zero.

Unfortunately, most publications still do not provide adequate distinction between the capture zone and the zone of pessure influence of a well. One of the most popular ground-water textbooks (Freeze and Cherry, 1979) makes no mention of such a distinction, or of capture zones generally. The same is true of a highly respected industry text (Driscoll, 1986). Todd (1980), does provides the mathematical description of a capture zone, but does not discuss the practical ramifications of its delineation. An EPA Handbook provides some discussion of capture zones (EPA, 1985), but it couches design recommendations primarily in terms of drawdown (water level declines caused by pumpage). It also does not carry the idea of capture zones over into key figures (e.g., Fig.'s 5-2, 5-3, 5-5, and 5-6 of EPA, 1985), leaving the reader a bit unsure of the message.

3. Well Spacings

When there are two or more pumping wells operating in unison, and they are spaced closely enough, their individual capture zones coalesce into a single collective capture zone. When that happens, the individual stagnation points coalesce into a *stagnation zone* that is shared by the wells. If the wells are not properly spaced, their individual capture zones will remain intact and the portions of the aquifer lying between adjacent capture zones will be free to move on downgradient (Keely, 1984). Similarly, when two or more injection wells are operating in unison, their individual rejection zones will coalesce to form a single collective rejection zone only if their spacing is appropriately close.

A number of approaches have been used to determine the optimal spacing of pumping and injection wells. The most traditional approach is the use of well hydraulics formulas to estimate the position and shape of the zone of pressure influence surrounding a well (Lohman, 1972; Todd, 1980; EPA, 1985; Driscoll, 1986). This information is usually obtained as point estimates of the drawdown caused by pumping wells or the pressure increase caused by injection wells. When taken together with pre-operational water levels, estimated drawdowns and pressure increases can be used to generate net/resultant water level elevation maps for the operating conditions of a pump-and-treat remediation. Capture zones and rejection zones are identifiable on net water level elevation maps by their elevation divides and closed contours; but the resolution of their positions by this approach is subject to a number of errors due to the imperfect nature of well hydraulics theory to date.

4. Well Hydraulics

The mechanics of pumping and injection wells have been studied intensively for a number of years, but there are still a number of gaps in the theories that describe their hydraulic effects. For instance, the Theis equation is completely satisfactory for describing the time-development of pressure changes induced by a flowing well in a confined aquifer, provided that the well is screened throughout the entire saturated thickness of the aquifer and that certain other assumptions are met. No such equation exists to describe satisfactorily the time-development of pressure changes induced by a flowing well in an unconfined aquifer (also, water-table or phreatic aquifer). Nor does an equation exist for the satisfactory description of partial penetration and partial screening effects in unconfined aquifers. The latter theoretical shortcomings are not inconsequential, since most pump-and-treat remediations involve the use of partially penetrating, partially screened wells in unconfined aquifers and therefore have varying hydrodynamic effects over time.

Numerical models can be used in lieu of the Theis equation or other analytical models to determine the effects of pumping and injection wells, and they offer the advantage of being able to incorporate complex aquifer boundaries; but numerical models have their limitations too. The ability to incorporate complex boundary conditions is useful only if one can establish accurately the type and orientation of the boundary. Moreover, numerical solutions are grid-block-by-grid-block discretized *approximations* of the real world, as opposed to the exact -- but highly simplified -- representations offered by analytical models. Numerical models allow for more sophisticated representations than analytical models, but they may incur errors (such as numerical dispersion and numerical oscillation) that are not encountered with analytical models.

Given the preceding, it may seem that neither the theories nor the tools exist to design properly pump-andtreat remediations; but this is not so. Rather, it is important to place what is known in perspective; the magnitude of errors arising from the simplifying assumptions of analytical models and the discrete approximations of numerical models must be understood and estimated on a site-specific basis. Just as importantly, the natural processes that control contaminant movement (e.g., advection, dispersion, sorption, biotransformation, etc.) must be identified and their relative roles estimated for each situation (Keely and others, 1986).

Conventional Pump-and-Treat (P&T) Remediations

Conventional remediations of ground-water contamination often involve *continuous* operation of an extraction-injection wellfield. In these remedial actions, the level of contamination measured at monitoring wells may be dramatically reduced in a moderate period of time, but low levels of contamination usually persist. In parallel, the contaminant load discharged by the extraction wellfield declines over time and gradually approaches a residual level in the latter stages (Figure 1). At that point, large volumes of water are being treated to remove small quantities of contaminants. Depending on the reserve of contaminants within the aquifer, this may cause a remediation to be continued indefinitely, or it may lead to premature cessation of the remediation and closure of the site. The latter is particularly troublesome because an increase in the level of ground-water contamination may follow (Figure 2) if the remediation is discontinued prior to removal of all residual contaminants.

There are several contaminant transport processes that are potentially responsible for the persistence of residual contamination and the kind of post-operational effect depicted in Figure 2. In order to generate such effects, releases of contaminant residuals must be slow relative to pumpage-induced water movement through the subsurface. Transport processes that generate this kind of behavior during continuous operation of a remediation wellfield include (i) diffusion of contaminants within spatially variable sediments, (ii) hydrodynamic isolation, (iii) sorption-desorption, and (iv) liquid-liquid partitioning.

1. Advection vs. Diffusion

Variations in rates of advection that are caused by spatial variability of hydraulic conductivity result in rapid cleansing of higher permeability zones by extraction wellfields, but only diffusion-controlled (slow) removal of contaminants from of low permeability zones (Figure 3). The situation is similar, though reversed, for in-situ remediations that require the injection and delivery of nutrients or reactants to the zone of intended action; access to contaminants in low permeability sediments is diffusively restricted.

4

Figure 1.

Figure 2.

1

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Figure 3.

The orders-of-magnitude greater surface area of the low-permeability sediments allows significantly greater amounts of contaminants to accumulate on them during the pollution event/activity, in contrast to much lower accumulations of contaminants in high permeability sediments. Hence, the majority of contaminant reserves may be available only under diffusion-controlled conditions in many heterogeneous settings.

2. Hydrodynamic Isolation

The operation of any wellfield in a moving aquifer results in the formation of stagnation zones downgradient of extraction wells and upgradient of injection wells. The stagnation zones are hydrodynamically isolated from the remainder of the aquifer, so mass transport within the isolated water may occur only by diffusion. If remedial action wells are located within the bounds of a contaminant plume, such as for the removal of contaminant *hot-spots*, the portion of the plume lying within their associated stagnation zones will not be effectively remediated.

3. Sorption Influences

For sorbing compounds, the number of pore volumes to be removed depends not only on the sorptive tendencies of the contaminant but also on whether flow rates during remediation are too rapid to allow contaminant levels to build up to equilibrium concentrations locally (Figure 4). If insufficient contact time is allowed, the affected water is advected away from sorbed contaminant residuals prior to reaching equilibrium and is replaced by fresh water from upgradient. This method of contaminant removal generates large volumes of mildly contaminated water where small volumes of highly contaminated water would otherwise result.

4. Liquid-Liquid Partitioning

When non-aqueous phase liquid (NAPL) residuals are trapped in pores by surface tension, diffusive liquid-liquid partitioning controls dissolution of the NAPL's into the ground water. Similar to the process with sorbing compounds, flow rates during remediation may be too rapid to allow aqueous saturation levels of the partitioned contaminant to be reached locally (Figure 5). If insufficient contact time is allowed, the affected water is advected away from the NAPL residuals prior to reaching chemical equilibrium and is replaced by fresh water from upgradient. Again, this process generates large volumes of mildly contaminated water where small volumes of highly contaminated water would otherwise result.

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Figure 4.

Figure 5.

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Figure 6.

Innovative P&T: Pulsed Pumping

Pulsed operation of hydraulic systems is the cycling of extraction or injection wells on and off in *active* and *resting* phases (Figure 6). The resting phase of a pulsed-pumping operation can allow sufficient time for contaminants to diffuse out of low permeability zones and into adjacent high permeability zones, until maximum concentrations are achieved in the higher permeability zones; or, for sorbed contaminants and NAPL residuals, sufficient time can be allowed for equilibrium concentrations to be reached in local ground water. Subsequent to each resting phase, the active phase of the pulsed-pumping cycle removes the minimum volume of contaminated ground water, at the maximum possible concentrations, for the most efficient treatment. By occasionally cycling only select wells, their stagnation zones may be brought into active flowpaths and remediated.

1. Special Considerations

Pulsed operation of remediation wellfields incurrs certain additional costs and concerns that must be compared with its advantages for site-specific applications. During the rest phase of pulsed-pumping cycles, peripheral gradient control may be needed to ensure adequate hydrodynamic control of the plume. In an ideal situation, peripheral gradient control would be unnecessary. Such might be the case where there are no active wells, major streams, or other significant hydraulic stresses nearby to influence the contaminant plume while the remedial action wellfield is in the resting phase. The plume would migrate only a few feet during the tens to hundreds of hours that the system was at rest, and that movement would be rapidly recovered by the much higher flow velocities back toward the extraction wells during the active phase.

When significant hydraulic stresses are nearby, however, plume movement during the resting phase may be unacceptable. Irrigation or water-supply pumpage, for example, might cause plume movement on the order of several tens of feet per day. It might then be impossible to recover the lost portion of the plume when the active phase of the pulsed-pumping cycle commences. In such cases, peripheral gradient control during the resting phase would be essential. If adequate storage capacity is available, it may be possible to provide gradient control in the resting phase by injection of treated waters downgradient of the remediation wellfield. Regardless of the mechanics of the compensating actions, their capital and operating expenses must be added to those of the primary remediation wellfield to determain the complete cost of pulsed pumping.

2. The Pulsed Purnping Project

EPA's Risk Reduction Engineering Laboratory in Cincinnati initiated a three-phased project for evaluation of the pulsed pumping technique in December of 1988. Administration of the project is overseen by the Center for Hazardous Waste Research at the University of Cincinnati, while the technical direction is the responsibility of Dr. Joseph F. Keely (Portland, Oregon). The primary objective of the study is to investigate the potential for the pulsed pumping method to improve the efficiency of contaminant removal and the cost-effectiveness of hydrodynamically-dependent remediations, specifically including both pump-and-treat operations and in-situ operations.

The Phase 1 efforts consist of reconnaissance surveys and preliminary computations. The results of these will be used to prepare a decision-support document for the Agency's use in determining the feasibility and attractiveness of sponsoring Phase 2 and Phase 3. Phase 2 concentrates on detailed analyses of pulsed-pumping operations at one or more Superfund sites where remediations have already commenced. Phase 3 is a field demonstration of pulsed pumping at an unremediated Superfund site, including all design and operation aspects.

The proposed approach to accomplishing the goals of Phase 1 consists of:

- (1) examination of the literature of several technological fields,
- (2) identification of candidate sites for Phase 2 and Phase 3,
- (3) preparation of conceptual designs for pulsed pumping operations, and
- (4) analysis and discussion of associated economic and technical aspects.

There is great need to review the literature from several technological fields. This can be done most efficiently by searching computerized databases, and this is planned. One should not underestimate the value of information not published in the scientific literature, however. The reports generated from investigations of hazardous waste sites, for example, are usually public documents that are rarely synopsized for trade journals and formal publications.

A number of remediations that are underway that incorporate some of the principles of pulsed pumping. For instance, pumpage from contaminated bedrock aquifers and other low permeability formations results in intermittent operation by default; the wells are pumped dry even at low flow rates. In such cases, the wells are operated on-demand with the help of fluid-level sensors that trigger the onset and cessation of pumpage. The latter is a far cry from the kind of optimization that is possible in a contaminant removal sense; the onset and cessation of pumpage need to be keyed to contaminant concentration levels. Nevertheless, the examination of RI/FS and other documents that describe on-demand systems in use at waste sites will provide useful information, and help to determine the criteria to be used in selecting candidate sites for Phase 2 and Phase 3.

The Agency's decision to proceed with Phase 2 and Phase 3 depends on the identification of candidate sites.

EPA's Regional Offices will be contacted by the project participants to discuss the project with site managers and to examine site documents. After careful review and cross-comparison of the information from the Regions, three Regions will be chosen for field visits. One or more sites in each Region selected will be visited and examined in detail, with video recording of current site conditions and activities, and interviews with responsible officials and site managers. Additionally, Dr. Keely's involvement in the Remediation Performance Project sponsored by EPA-RSKERL (and other consulting ventures) will provide additional opportunities to visit promising sites.

Work on the candidate sites will include preparation of conceptual designs of pulsed-pumping scenarios for each. These will be explored with computer simulations; e.g., by examining combinations of extraction wells and injection wells under hydrogeologic assumptions appropriate to the respective sites. Note that while the computer simulations will generate useful insights, the programs used to generate them are based on idealized theoretical assumptions (e.g., instantaneous contact of contaminants with all waters of a certain stratum). The result is that clean-up efficiencies predicted by conceptual simulations will likely exceed what is achievable in reality. For that reason, the Phase 1 simulations are to be used primarily to optimize generalized wellfield design strategies and economic trade-offs. Intensive modeling efforts are reserved for analysing and fine tuning selected Superfund remediations in Phase 2, and for design and management of a field demonstration at an unremediated site in Phase 3.

Monitoring the Performance of P&T Remediations

There are serious unresolved questions about how one ought to monitor the performance of pump-and-treat remediations. Neither contaminant distributions nor velocity distributions are constant throughout the *zone of action* (that portion of an aquifer that is actively being manipulated by the pumping wells). Consequently, monitoring strategies must be cognizant of the need to detect rapid, sporadic changes in the quality of ground water at any specific point in the zone of action. What this means in practice is that tracking the effectiveness of pump-and-treat remediations is quite complicated chemically. The frequency and density of samplings must consider the detailed flowpaths generated by the remediation wellfield, including the variations in susceptibility to transport processes along those flowpaths. It also means that it may be necessary to move the chemical compliance points (or *corrective action monitoring* points) during the course of a remediation.

Nor are evaluations of the hydrodynamic performance of remediation wellfields easily accomplished. For example, it is usually required that an inward hydraulic gradient be maintained at the periphery of a contaminant plume. This requirement is imposed to ensure that no portion of the plume is free to migrate away from the zone of action. To assess this performance adequately, the hydraulic gradient must be measured accurately in three dimensions between each pair of adjacent pumping or injection wells. The design of an array of *piezometers* (small diameter wells with very short screened intervals, that are used to measure the pressure head of selected positions in an aquifer) for this purpose is not as simple as one might first imagine. Two points define a line, and three points define a plane; but many more are needed to define the convoluted surface that develops between adjacent pumping or injection wells. Not only are there velocity divides in the horizontal plane near active wells, but in the vertical plane, too, because the pressure influence of each well extends to only a limited depth in practical terms.

Principles for the practical use of remediation wellfields and other ground-water clean-up technologies are thus evolving still, and are highly dependent on site-specific knowledge of the influence of transport processes on contaminant levels. There is still much to be learned about how to design and implement highly specific and cost-effective remedies. Far more could be accomplished than is typically done, however, if the transport processes that govern the environmental behavior and treatability of contaminants were investigated actively at each site. The past history of conducting a bare minimum of field characterization efforts (other than chemical samplings) has not led to complete or satisfactory remediations, generally. Such approaches appear penny-wise / pound-foolish in retrospect, and are yielding to transport-process-intensive approaches as the ground-water profession strives for meaningful improvements in the specificity and cost-effectiveness of remediations (Keely and others, 1986).

There are a lot of misconceptions and misunderstandings regarding the effects that key hydrodynamic, abiotic/chemical, and biological processes have on the transport and fate of contaminants in the subsurface. Some of these, such as the confusion over capture zones and drawdown cones of pumping wells that was discussed earlier in this document, are relatively easy to address by educational efforts. Others, such as the controversy over just what hydrodynamic dispersion is in a physical sense, or the way that sorption and biotransformation rate constants ought to be derived and subsequently used in predictive models, can be addressed only by applied research.

1. Compliance Criteria

Extraction and injection wells used in ground-water contamination remediations produce complex flow patterns, where previously there were comparatively simple flow patterns. Historical trends at local monitoring wells are thereby rendered useless when remediation commences. The complex flow patterns generated by remediation wellfields present great challenges in terms of characterization of the altered transport pathways. Hence, there is often a need for more data to be generated during the remediation than were generated during. the entire RI/FS process at a site, and for those data to require much more sophisticated interpretations. The key controls on the quality of data obtained for interpretations are the compliance criteria that are selected and the compliance point locations at which those criteria are to be applied.

It is essential to recognize the many kinds of compliance criteria actually in use today. There are three major kinds of compliance criteria: chemical, hydrodynamic, and administrative control. Chemical compliance criteria are MCl's, ACL's, Detection Limits, and Natural Water Quality. Hydrodynamic compliance criteria are such things as (i) demonstrated prevention or minimization of infiltration through the unsaturated zone, (ii) maintenance of an inward hydraulic gradient at the boundary of a plume of ground-water contamination, and (iii) providing minimum flows in a stream. Administrative control compliance criteria include (i) effective implementation of drilling bans and other access- limiting administrative orders, (ii) proof of maintenance of site security, and (iii) reporting requirements, such as frequency and character of operational and post-operational monitoring. Almost any combination of chemical, hydrodynamic, and administrative control compliance criteria may be appropriate for a specific compliance point, depending on its location.

The most widely known kind of compliance point is located a short distance downgradient of the plume. The exact location is chosen so that: (i) it is neither in the plume nor in adjacent areas that may be affected by the remediation, (ii) it is in an uncontaminated portion of the strata through which the plume would migrate if the remediation failed, and (iii) its location minimizes the possibility of detecting other actual or potential sources of contamination (e.g., it is not located too far away, to be relevant to the target site only). Data gathered there serve to indicate *out-of-control* conditions when a portion of the plume escapes the remedial action. The compliance criteria typically specified for this kind of compliance point are Natural Water Quality (Background) or Detection Limits. This kind might be referred to as a Background Compliance Point.

Another common kind of compliance point is represented by existing public water supply wells downgradient of a plume. The locations of these points are not negotiable; they are where they are. The significance of their use is in assuring the quality of water delivered to consumers, as it relates to specific contaminants associated with the target site. The compliance criteria typically specified for this kind of compliance point are MCL's, MCLG's, and maintenance of existing quality. An appropriate name for this kind is Public-Supply Compliance Point.

A third kind of off-plume compliance point commonly established is one for determinations of hydraulic gradients. This kind is comprised of a cluster of small diameter wells that have very short screened intervals, and is usually located just outside the perimeter of the plume and along a line running between two plume remediation wells. Water level elevations are measured and used to prepare detailed contour maps from which determinations of the direction and magnitude of the local hydraulic gradients can be made. This kind might be referred to as Gradient Control Compliance Points.

Less commonly known is the kind of compliance point represented by monitoring wells located within the perimeter of the plume. Most of these are installed during the site investigation phase (prior to the remediation), but others may be added subsequent to implementation of the remediation; they are used to monitor the progress of the remediation within the plume. These can be subdivided into compliance points located on-site (within the property boundary of the facility that contains the source of the plume of contamination), and those located off-site (beyond the facility boundary, but within the plume); the latter kind assumes that the plume has migrated beyond the facility boundary.

Because of its proximity to the source of contamination, and the technical infeasibility of complete removal of the source at many sites, the compliance criteria for an on-site compliance point range from Natural Water Quality to Alternate Concentration Limits that represent the best that can be done cost-effectively. In addition, hydrodynamic compliance criteria are often associated with on-site compliance points; e.g., moisture-content determinations may be used to evaluate the effectiveness of a cap in reducing or eliminating infiltration through contaminated soils in the unsaturated zone. An explicit name for these is On-Site Plume Compliance Point. Similarly, one can refer to the remaining compliance points located within the perimeter of the plume as Off-Site Plume Compliance Points. The compliance criteria applied to these tend closer to Natural Water Quality than is the case on-site, but again are closely tied to technology-driven ACL's; more stringent criteria are usually appropriate, because the source is not included.

As discussed in the preceding paragraphs, each kind of compliance point has a specific and distinct role to play in evaluating the progress of a remediation. The information gathered is not limited to chemical identities and concentrations, but includes other observable or measurable items that relate to specific remedial activities and their attributes. In choosing specific locations of compliance points, and criteria appropriate to those locations, it is essential to recognize the interdependency of the compliance criteria for different compliance points. For example, one cannot justify liberal ACL's on-site and have realistic expectations of meeting more stringent ACL's off-site; the facility boundary will not magically dilute the residual contaminants leaving the on-site area after the remedial action ceases operation. Similarly, one cannot expect Background Compliance Points to remain free of contamination if the off-site plume ACL is chosen inappropriately.

In addition to the foregoing, one must decide what method(s) should be used to determine statistical variations in each parameter measured, what cut-off(s) should be applied (e.g., 95% confidence interval), whether they apply to each compliance point or can be averaged, what method to use to indicate that the maximum clean-up has been achieved (e.g., the zero- slope approach), and so on.

2. The Remediation Performance Project

The National Center for Ground Water Research (NCGWR) develops and disseminates information on the transport and fate of contaminants in the subsurface. NCGWR's activities are funded through EPA's R.S. Kerr Environmental Research Laboratory (RSKERL), which has a similar mission with respect to contamination of the subsurface. The Remediation Performance Project is a multi-phase effort initiated by RSKERL to increase the availability of information about strategies and data presentation/interpretation methods useful for evaluations of the ongoing performance of ground-water contamination remediations.

Phase 1 of the Remediation Performance project began 1 August 1987 and is scheduled for completion by 31 December 1988. The Phase 1 tasks are focused on collecting information about the adequacy of monitoring networks and compliance criteria now in use at Superfund sites, and about the manner in which the resulting data are interpreted and presented for decision making. Special emphasis is also being placed on transport-process data needs in the use of assessment models for decision making.

Phase 2 focuses on development of the Remediation Operational-Performance Evaluation Methodology (ROPEM) by which monitoring well network designs and compliance criteria can be selected and used effectively, so that the ongoing performance of a remediation can be tracked accurately. ROPEM will provide worked examples and recommendations for the use of mathematical modeling (e.g., flowline analyses, mass balances, boundary influences), statistical analyses (e.g., regressions, correlations, ANOVA), graphical analyses (e.g., phase diagrams, Stiff plots, Piper diagrams), and theoretical approaches (e.g., structure-activity relationships, sedimentology, geomorphology). The potential power of ROPEM will be illustrated by applying it to existing Chem-Dyne and United Chrome Products Superfund sites' data; this will include calibrating mathematical models to both sites, as well as performing statistical and graphical analyses on data from these sites.

Complete field validation of ROPEM will require enhanced characterization of these or other sites. Specifically, the enhanced site characterization should lead to a detailed understanding on the transport pathways, the mass of contaminants in reserve on subsurface solids, the total organic carbon content of those solids, and the susceptibility of indigenous organisms to engaging in biotransformation of the contaminants. Such characterization efforts provide the optimal level of transport process data recommended by ROPEM. These and other field evaluation activities are reserved for Phase 3.

References



Figure 2. Potential ground-water contamination response to cessation of continuous pumpage. The three year window is a typical regulatory criterion for maintenance of minimum remediation concentrations for site closures.



Figure 1. Effluent Concentration Pattern for Continuous Wellfield Operations



Figure 3. Diffusive release of contaminants from low permeability sediments to adjacent high permeability sediments



Figure 4. Concentration of ground-water contaminants controlled by de-sorption kinetics



GROUNDWATER VELOCITY

Figure 5. Dependence of ground-water contamination level on partitioning of non-aqueous phase (P) residuals as a function of increasing ground-water velocity



Figure 6. Effluent concentrations for a pulsed pumping remediation. Residual and maximum contaminant levels decline with each cycle.

IN-SITU SOIL WASHING AND FLUSHING TECHNOLOGIES

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PRESENTATION OUTLINE

IN SITU SOIL WASHING AND FLUSHING TECHNOLOGIES

Physical Properties and Behavior of Creosote Oil

- o Physical properties
- o Occurrence and distribution
- o Pore space saturation
- o Effects of pore saturation on permeability

Primary Recovery of Creosote Oil

- o Literature review
- o Design concepts
- o Laramie Tie Plant case study
 - -- 1987 field pilot
 - -- 1988 system scale up

Enhanced Removal of Creosote Oil

- o Review of potentially applicable techniques
- o Surfactant systems
 - -- Reduction of interfacial tensions
 -- Mobility ratios
- o Laboratory studies
- o Environmental concerns
- o Laramie Tie Plant case study
 - -- 1988 field pilot -- 1989 system scale up

Summary

- o Evaluation of feasibility at other sites
- o Estimation of costs

IN SITU REMOVAL OF WASTE WOOD-TREATING OILS FROM SUBSURFACE MATERIALS

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PRESENTED AT THE U.S. EPA FORUM ON REMEDIATION OF WOOD-PRESERVING SITES, OCTOBER 1988, SAN FRANCISCO

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INTRODUCTION

A common condition at wood-treating facilities is soils and/or aquifer materials contaminated by waste wood-preserving oils. Contamination may vary from soil stained black with residual oils to areas in which oils will freely flow from the soils into a well. Often these contaminated materials occur at depths or in volumes that limit the feasibility of excavation and at concentrations that limit the effectiveness of pumpand-treat remediation strategies. Under these conditions, in situ technologies can be applicable for site remediation. This paper discusses in situ methods for removal of waste wood-preserving oils from the subsurface using waterfloods and enhanced recovery technologies.

In 1980, researchers estimated that 631 active wood-preserving facilities existed in the United States. In addition to these active facilities, thousands of other wood-treating facilities have been abandoned. Primary materials used to treat wood products at these facilities fit into the categories of creosote, pentachlorophenol, and arsenic-based systems. Of these, pentachlorophenol and creosote systems are oil based while the arsenical systems are water based. Contamination is more commonly associated with pentachlorophenol and creosote systems due to greater periods of historical use, a higher overall volume of use, and the formation of oil water emulsions during wood treatment.

Wood preservatives are commonly forced into wood products in pressurized retorts. As the oil-based systems move into the wood products, water is displaced from the wood, commonly forming an oil-water emulsion with the wood-treating oils. Historically, these emulsions have been managed, as per the standards of the era, in facilities such as unlined ponds which often allowed waste wood-treating oils to migrate to subsurface materials. Other potential sources of subsurface contamination at wood-treating facilities include drip pads without collection systems, leaking tanks, leaking pipelines, and fluids spilled during liquid transfers.

Once they are in the subsurface materials, the waste oils sink through unsaturated porous media and tend to become perched above strata of low permeability. Creosote systems are typically denser than water, therefore, they tend to continue sinking through saturated porous media until they reach a low permeability boundary. Once at this boundary, if it exists, further migration of creosote-based woodpreserving oils is governed by the topography of the boundary. The oils often accumulate within topographic lows. Pentachlorophenol systems are typically less dense than water; therefore, they tend to accumulate on top of the water table.

DEN/109R/002

Removal of waste wood-treating oils from subsurface materials is often one of the primary obstacles to cleanup of woodtreating facilities. The remainder of this article focuses on recovery of creosote-based waste wood-treating oils from subsurface materials. Although this is the focus, much of the information also applies to other types of oil contamination in porous media. Specifically discussed are: (1) the physical properties of creosote-based wood-treating oils and how they impact remediation, (2) the design concepts and potential effectiveness of waterfloods, and (3) the potential for using enhanced recovery methods including, surfactant-based waterfloods. Where applicable examples are presented from laboratory and field studies.

PHYSICAL PROPERTIES AND BEHAVIOR OF CREOSOTE OIL

Prior to a discussion of methods for recovery of creosotebased waste wood-treating oils, an understanding of contaminant mobility and distribution, based on the physical properties of the oils, needs to be developed.

Creosote-based wood-preserving oils are derived from fractional distillation of coal tars produced during coking of coal. The oils contain a complex mixture of polynuclear aromatic hydrocarbons (PNAs), primarily consisting of two, three, and four fused-ring organic compounds. In addition, creosote-based wood-treating oils either contain or are mixed with a large fraction of carrier oils, consisting primarily of aliphatic hydrocarbons. The carrier oil fraction enhances the penetration of the PNA compounds into wood products during treatment.

Typical creosote based oils are denser than water (e.g., 1.02 to 1.04 g/cm³). Consequently, the oil will sink within water saturated porous media given sufficient volumes of oil and formation permeability. Viscosities observed by the authors have been in the range of 50 and 70 centipose (approximately 50 to 70). This causes the oils to flow slower than water under an equivalent gradient. In addition, the oil is highly immiscible with water which causes the oils to be immobile within porous media except when present at high concentrations.

The degree of oil saturation within the pore space of the alluvium, affected by the oil's viscosity and immiscibility with water, plays a critical role in defining the oil's mobility. Laboratory work performed by MTARRI and Surtek, Inc., both of Golden, Colorado, defined the fraction of oil present in an alluvial sand that is recoverable and the effect of oil saturation on permeability with respect to oil and water. The laboratory work consisted of bench-scale linear core floods using coarse sands and oil from a wood-treating site. The procedure involved sequential flooding of the soil cores with water, with oil, and finally with water again. The following results were obtained:

- o The maximum oil saturation that could be achieved during oil flooding of the cores was about twothirds of the pore space. The other one-third of the pore space remained filled with water, which was held to the sand grains, immobile under an oil flood (referred to as residual water).
- After the oil flood, a waterflood of the cores could displace about one-half of the oil present, leaving about one-third of the pore space filled with oil. This oil was held in place primarily due to the interfacial tension between the fluids and the capillary forces associated with the aquifer matrix (referred to as residual oil).

Overall, the data indicate that in a coarse sandy soil, waterfloods can achieve a maximum 50 percent reduction in free-phase oil. Figure 1 graphically presents these results.

During the core floods, the relative permeability of the cores with respect to oil and water as a function of pore saturation was also determined. These data indicated:

- o The formation permeability with respect to oil is at a maximum when the oil saturation of the pore space is at a maximum. This finding is important in that the mobility; therefore, the recoverability of the oil is greatest when the formation permeability with respect to oil is at a maximum.
- Formation permeability with respect to water is at a maximum when water saturation of the pore space is at a maximum. This finding is also important: to maximize water production from a given interval, oil saturation should be at a minimum.

Figure 2 presents the observed impact of oil pore saturation on formation permeability. Intuitively, the described results bear out: with lower fluid saturations, the cross-sectional area for flow decreases and the tortuosity of the flow path increases.

FIGURE 1 LINEAR CORE FLOOD RESULTS DISTRIBUTION OF OIL/WATER IN PORE SPACE





PRIMARY OIL RECOVERY

Where creosote-based wood-preserving oils are present above residual saturation, primary oil recovery may be an appropriate step in remediation of contaminated subsurface materials. The overall concept is similar to recovery techniques used in the petroleum industry, involving the use of waterfloods to move oil to a recovery point.

Through primary or waterflood recovery, further migration of free-phase oil can be inhibited and the volume of subsurface contaminants can be reduced. In addition, oil recovery through waterflood techniques may be an effective "first step" in a more thorough cleanup of subsurface contamination through use of more complex, enhanced in situ removal/treatment technologies. A review of some of these technologies is presented later in this paper.

FLOW-PATH MANAGEMENT

Efficient recovery of oils from porous media through fluid delivery and withdrawals requires effective management of the flow path along which the oils will be drawn toward the recovery system. For oil to move toward a recovery system, a gradient must be present and a continuous body of material with sufficient permeability must exist for the oil to migrate through. Simply stated through Darcy's equation, oil flow is equal to formation permeability with respect to oil, multiplied by cross-sectional area available for flow, multiplied by the flow gradient. The limiting of any one of these variables will severely restrict the efficiency of a waterflood recovery system.

Flow gradients toward a recovery system are typically established through pumping water from the formation in the vicinity of the oil-recovery system. Formation permeabilities with respect to oil can be optimized by maintaining a maximum formation saturation with respect to oil through the interval in which the oil will migrate. This optimization can be accomplished by allowing the oil to accumulate in a fixed interval that coincides with the oil-recovery flow path. Sufficient saturated thickness of the oil recovery flow path can be maintained by controlled pumping of water and oil from separate recovery systems at rates that prevent the flow of the less viscous, more mobile water from truncating the flow of the viscous oil.

An additional consideration in the management of the recovery flow path is the limitations of oil movement into areas that have not been previously unwetted by oil. As oil is drawn into unwetted areas, large amounts of oil are retained by the soils. The capacities of the soils to retain oil must be satisfied before the flow of oil through the materials will occur. Since residual adsorption capacities of soils can be in the neighborhood of one-third of pore space, this limitation can result in the loss of large volumes of mobile free-phase oils that might have been recovered had they been kept outside of unwetted areas. Another disadvantage of moving oils into unwetted areas is that it increases the volume of soils at residual saturation which may require further, potentially expensive remediation.

PRIMARY OIL RECOVERY CASE STUDY

Faced with the need to recover creosote-based waste woodtreating oils from a shallow, alluvial aquifer in the western United States, CH2M HILL designed, operated, and evaluated a recovery system using the above concepts. The following text reviews the system design and pilot test results. Additional information can be found in Sale, et al. (1988).

CH2M HILL's first step in addressing recovery of oil from the site was to investigate the existing recovery system. This system used single pumps in large-diameter wells. When oil accumulated in the wells, the pump would operate until the oil was purged from the well. Over the system's 3-year operational period, limited production was achieved. Factors limiting oil production include:

- o The pumps operated infrequently; therefore, the only forces moving oil to the recovery wells were gravity and the local groundwater gradient.
- Fluids were forced to flow into the wells through a restricted screen at the base of the alluvium.
 During pumping, the flow of the more mobile water effectively truncated the flow of oil in the restricted screen interval.

Based on the limited success of the existing system and the understanding of its shortcomings, CH2M HILL developed and field tested an innovative oil recovery system. The general objectives of the pilot test were (1) to evaluate the feasibility of recovering the mobile creosote-based wood-treating oils from the shallow aquifer at the site and, if successful, (2) to obtain sufficient design data to proceed to a scaled-up or full-scale primary oil-recovery system design.

Dual Drainline Design Concept

Fluids could be pumped from the alluvium using either wells or drainlines. To overcome the limited fluid production that could be achieved in the shallow alluvium, we used horizontal drainlines instead of wells for fluid recovery. For recovery of the viscous, denser-than-water, immiscible creosote-based wood-treating oil, we selected a system of dual drainlines to optimally manage oil and water flow and formation saturations.

Diagrams A through D in Figure 3 present cross sections that depict site conditions and the hydraulic concepts associated with the dual drainline system. Diagram A shows fluid distribution under static conditions and the physical location of the drainlines. In this case, concentrated waste woodpreserving oil has accumulated at the base of the alluvium and is overlain by water.

Diagram B shows the fluid distribution with only the lower oil recovery drain (ORD) being pumped. Under this stress, water and oil are produced, but the majority of the pore space surrounding the ORD is occupied by water. This condition limits the formation permeability with respect to oil and effectively truncates or limits the flow of oil to the ORD.

Diagrams C and D outline the dual drainline approach, which overcomes the drawback of truncated flow illustrated in Diagram B. In Diagram C, only the water table depression drainline (WTDD) is being pumped. It produces primarily water and induces a hydraulic flow gradient in the underlying oil-saturated portion of the aquifer. Because oil saturation in the lower portion of the aquifer is at its maximum, the formation in this interval has its highest potential permeability with respect to oil. The oil's mobility within the formation is optimized (1) by the gradient that results from pumping the overlying water, (2) by the formation's optimal permeability to oil that results from not drawing water through the oil-saturated interval, and (3) by the increased thickness of the flow path available for oil migration.

The net result of pumping only the WTDD is that oil is drawn toward and accumulates beneath the WTDD. Diagram D shows the combined pumping of the WTDD and the ORD. If flow rates are properly managed, this combination results in the oil drawn toward the recovery system (through pumping the WTDD) being removed as it accumulates (through pumping the ORD).

Another advantage of the dual drainline approach is that a large degree of the needed oil-water separation is accomplished below ground. This minimizes the requirements for aboveground oil-water separation facilities.

Pilot Test Results

This design concept was tested in a pilot-scale application at a wood-preserving site. The actual ORD and WTDD installed at the site were constructed of 15-foot lengths of 4-inch



FIGURE 3 DUAL DRAINLINE CONCEPT slotted PVC pipe. The WTDD and ORD were located approximately 8 and 10 feet below grade. Materials present in the alluvium range from fine-grained sands and silt at the surface to coarse gravel at the base, which is located about 10 feet below grade. Underlying the alluvium is a silty, shale, which acts as a barrier to vertical migration of the wood-treating oils.

During the 29-day primary oil recovery pump test, 10,300 gallons of wood-treating oil (with a water content of less than 0.1 percent) were recovered. In addition, about 770,000 gallons of water were produced, treated, and recharged into the alluvial aquifer. Figure 4 shows cumulative oil and water production.

Pumping rates from the WTDD and ORD were varied during the test to gain information about optimum system operation and hydraulic responses of oil and water in the aquifer to different pumping stresses. Initial pumping rates of 11.3 gallons per minute (gpm) from the WTDD and 1.2 gpm from the ORD were selected, based on a trial run conducted during system checkout.

Pumping rates from the WTDD were increased 6 times during the test to a maximum rate of 40 gpm. The 40-gpm rate, which was approximately 2.6 gpm per foot of drainline, potentially represents the flow rate at which the oil-water interface between drainlines became unstable, causing oil and water layers to mix regardless of their densities.

Oil production from the ORD varied because of differences in formation conditions and different rates of water production from the WTDD. In general terms, the oil-productionversus-time graph (Figure 4) shows the following:

- Oil production rates exceeded 400 gallons per day (gpd) for the first 2 test days. This comparatively high rate reflects oil recovery in the immediate vicinity of the drainlines.
- Increases in oil production corresponded to increases in pumping from the WTDD. This correspondence suggests that operation of the WTDD enhanced oil migration toward the ORD.
- Oil recovery rates generally declined with time after system startup and after each increase in the WTDD pumping rate. This decline reflects oil depletion in the immediate vicinity of the recovery system as oil is drawn from greater distances.

CUMULATIVE WATER PRODUCTION VS. TIME





AND WATER PRODUCTION

- Oil production rates remained above 200 gpd at the end of the test, suggesting a strong potential to sustain production for periods beyond the 29-day pump test.
- o The average recovery rate was 357 gpd throughout the test. This rate indicates that where creosote oil occurs above residual pore saturation, the oil is mobile and can be recovered.

Based on the results of the pump test, a larger system was installed and operated at the site. In a period of 4 months, this system recovered 220,000 gallons of waste creosote-based wood-treating oils from an area of approximately 2 acres.

IN SITU SOIL FLUSHING

A limitation of waterflooding or primary oil recovery is that only a portion of the total free-phase oil in the subsurface can be removed, leaving a substantial residual oil level in the subsurface. Due to the low solubility of the residual creosote-based wood-treating oils and their presence in percent concentrations, residual oil can act as a long-term source of groundwater contamination.

This section covers factors that limit the effectiveness of waterflooding. Enhanced oil removal methods, also called in situ soil washing, which may be effective in achieving lower residual contaminant levels are also described.

FACTORS AFFECTING RESIDUAL OIL CONCENTRATIONS

Three primary factors contribute to the significant residual oil concentrations remaining after waterflood oil recovery, and make this residual difficult to flush from the subsurface. These factors are (1) the water solubility of wood-preserving oils; (2) interfacial tension (IFT) between the oil, water, and soil; and (3) the relative permeability of oil and water.

The low solubility of residual creosote oils limits the effectiveness of water based soil flushing methods because the amount of oil that dissolves into water and is flushed from the subsurface is insignificant in comparison with the residual oil left in place.

IFT can be described as the unbalanced forces acting on a droplet of free-phase hydrocarbon contamination. The lower the IFT, the greater the tendency of the droplet to be miscible in groundwater. The result of high IFT is the retention of the hydrocarbon on soil particles as opposed to its movement when groundwater is swept through the soil pores. Relative permeability can be described as the tendency of a porous system to selectively conduct one fluid when two or more fluids are present. The mobility ratio is the term used to describe the effects of relative permeability in the enhanced oil recovery industry. The mobility ratio is defined as:

$$m = \frac{K_D / U_D}{K_O / U_O}$$

where:

m = Mobility ratio
K_D = Effective permeability with respect to the
displacing fluid
K₀ = Effective permeability with respect to the oil
U₀ = Viscosity of the displacing fluid
U₀ = Viscosity of the oil

The higher the mobility ratio, the greater the tendency of the displacing fluid to flow around rather than push out the residual oil.

ENHANCED OIL-REMOVAL METHODS

Methods that have been developed or are considered for enhanced removal generally are based on overcoming one or more of the three factors described above. Many of these methods are adaptations of techniques developed for use for enhanced oil recovery (EOR) in the petroleum industry. These methods include:

- o In situ solvent extraction
- o Hot water or steam flooding
- o Carbon dioxide flooding
- o Surfactant flooding
- o Alkaline flooding
- o Polymer flooding

Each of these methods is briefly described below.

In Situ Solvent Extraction

In situ solvent extraction involves flooding the subsurface zone containing the residual oil with an organic solvent or water containing an organic solvent. This technique is based on increasing the solubility of the residual oil in the fluid used for flushing the subsurface. This method is not generally considered highly feasible for the following reasons:

 Environmental concerns regarding injecting organics that are effective as solvents into the subsurface

- o Residual solvents left in the subsurface
- Difficulties in treating fluids withdrawn from the subsurface that contain miscible mixtures of water, solvent, and oil
- High project costs for implementation

Thermal Methods

The most commonly considered thermal methods are hot water flooding and steam flooding. These methods rely on decreasing the residual oil level by increasing contaminant solubility and achieving a more favorable mobility ratio. Contaminant solubility in the soil flushing solution is increased because the water solubility of many organics increases at higher water temperature. More importantly, the viscosity of freephase hydrocarbon decreases with increasing temperature. Hydrocarbon recovery increases with decreasing viscosity because of the corresponding decrease in the mobility ratio.

A major limitation in the use of thermal methods is that at increased temperatures, denser-than-water free-phase oil may be converted to a floating oil. The adverse effect of this condition is that oil initially confined to a narrow lens may float through and wet previously uncontaminated portions of the subsurface. Costs may also be high due to the heat loss that occurs as large volumes of subsurface materials are heated.

The effectiveness of this technology in environmental applications is unknown.

Carbon Dioxide Flooding

Carbon dioxide flooding is an EOR technique that relies on achieving a decreased mobility ratio. Carbon dixoide is injected under pressure into an oil bearing zone. The viscosity of the oil decreases as carbon dioxide dissolves into the oil. Because this method relies on high pressures, it would only be applicable at relatively large depths in a confined strata.

The effectiveness of this technique in environmental applications is not known.

Surfactant Flooding

Soil flushing with surfactant solutions to extract hydrophobic organic contaminants appears to be one of the most promising of in situ cleanup technologies. Aqueous surfactant solutions are superior to water alone in extracting hydrophobic contaminants. Both the detergency of aqueous solutions and the efficiency by which organics are transported by aqueous solutions are thought by researches to be improved by surfactant addition. The processes for improving the detergency of aqueous solutions are preferential wetting, increased contaminant solubilization, and enhanced contaminant emulsification (Envirosphere, 1983). The addition of surfactants is thought to increase the efficiency by which organics are transported in aqueous solutions by lowering the interfacial tension between the aqueous and contaminant phase, which facilitates the distortion of spherical oil droplets as they pass through the soil.

Another reason the use of surfactants for in situ soil washing applications appears promising is that numerous environmentally safe and relatively inexpensive surfactants are available commercially (Wagner and Kosin, 1984).

Alkaline Flooding

EOR research has identified an IFT reduction method that may be much more cost-effective than the use of surfactants. When in contact with certain hydrocarbon mixtures, alkaline agents (e.g., sodium carbonate) can react to form surfactants via a saponification reaction. Because these surfactants are created at the aqueous-hydrocarbon interface, they can effectively reduce the IFT. The use of a combination of alkaline agents and surfactants may be the most costeffective way to reduce IFT and to enhance hydrocarbon recovery (Cooke et al., 1974; Krumrine et al., 1980).

As in surfactant flooding, IFT reduction through the use of alkaline agents is not likely to be effective if unfavorable mobility ratios still exist. Other potential problems with the use of alkaline agents may result from the high pH and reactive nature of these solutions. These problems include precipitation and resultant aquifer plugging, dispersal and expansion of clays, and leaching of trace metals.

Polymer Flooding

Another commonly used EOR method that may have environmental applications is polymer flooding. The oil-removal effectiveness of the waterflood can be increased by adding polymer to the water, which increases the viscosity of the flood and thus lowers the mobility ratio.

This method has not been evaluated extensively for use in environmental applications.

ASP Flooding

One combination of the techniques described above that has undergone limited testing for environmental applications is alkaline/surfactant/polymer (ASP) flooding. The addition of an alkaline agent and a surfactant address IFT; the addition of a polymer gives the flood a favorable mobility ratio. In bench-scale tests, an ASP flood was highly effective in displacing residual waste wood-preserving oil from a subsurface sandy soil (Kuhn et al., 1988).

IN SITU SOIL-WASHING APPLICATIONS

Case Studies

The majority of the work conducted to date regarding enhanced in situ recovery of oily subsurface contamination has focused on the use of surfactants. Published work conducted by American Petroleum Institute (API) (1979 and 1985), The Ellis (1984), and Tuck (1988) has demonstrated on a laboratory scale that surfactant systems are effective in removing large percentages of the residual oils present after waterflooding. Briefly primary findings of these studies include:

- API (1979) -- Residual oil saturation can be reduced using surfactant flooding on a laboratory scale.
- API (1985) -- Application of a surfactant to sandbox scale-model aquifer underscored the difficulties of optimally delivering the solutions to the oily intervals.
- Ellis (1984) -- Ninety percent cleanup levels using surfactant systems support the need for field demonstration.
- Tuck (1988) -- The efficiency of in situ soil washing can be enhanced using surfactants on a laboratory scale.

The only published field demonstration of in situ oil washing, known by the authors, was conducted at Volk Air Force base in Wisconsin by the EPA (1987). Results indicated no effective recovery of residual oils in a field application despite favorable results in the lab. The difference between lab success and field failure at the Volks site is interpreted as the difference in hydraulic flow conditions achieved in the laboratory core flood versus the far less controlled flow conditions in the field application.

A field soil washing pilot involving an ASP system is being performed; however, no data on this test are available.

Potential Limitations

Additional issues pertinent to the potential of soil-washing systems include: (1) compatibility of the soil-washing solution with the contaminated materials, aquifer skeleton, and native formation water, and (2) the required level of effort associated with treatment of the produced fluids.

Incompatibilities between the soil washing solution and the subsurface materials can potentially result in negative impacts. Chemicals used to enhance mobilities, such as alkaline agents, can lead to the precipitation of inorganics, such as calcium carbonate. If this happens on a large scale, the inorganics can plug the formation, limiting the feasibility of further in situ remediations that rely on soil flushing. Conversely, some proposed soil-washing systems could lead to unfavorable leaching of trace metals. This condition could result in trading organic contamination for inorganic contamination. Still another issue is biological fouling of an aquifer. Common components of soil washing systems are readily biodegradable. If in situ biodegradation of the soil washing system occurred extensively in the formation, the pore space could be plugged with biomass.

Treatment of fluids withdrawn from the subsurface in the in situ soil-washing process is also an issue. Surfactantbased soil-washing systems tend to form oil-water emulsions with the recovered oils. Separation into distinct phases can be difficult, especially when the density differences are small, as in the case of creosote-based wood-treating oils and water. If the oils and aqueous fractions cannot be isolated, then reuse of either the oil or the soil washing solution will be difficult. Costly options, such as biological treatment of produced fluids in an aboveground reactor, may be required.

Conceptual Design of In Situ Soil-Washing Systems

Despite the lack of hard field data defining the feasibility of surfactant-based in situ soil washing, the technology does offer opportunities for remediation of subsurface materials contaminated with residual concentrations of oily woodtreating wastes. Through in situ soil washing, the potential exists to remove 80 percent or more of the residual oils, thus reducing the contaminant source volume. In the case of in situ bioreclamation, the benefit of such a reduction would be a corresponding decrease in time and oxygen-demand requirements, a significant benefit for a potentially lengthy and expensive remediation method.

Probable process components needed to implement an in situ. soil-washing program include:

- Soil-Washing Solution Mixing. Except for smallscale applications, mixing the soil-washing solutions onsite will probably be cost-effective.
 Facilities could include storage tanks, mixing pumps, and filters capable of removing suspended solids that could plug the formation.
- Subsurface Delivery System. An important aspect of in situ soil washing is the effective delivery of the soil-washing solution to the interval in which the residual oil occurs. This delivery can be accomplished through drainlines, wells, trenches, or infiltration trenches. The most effective type of delivery system will be a function of sitespecific conditions. In all cases, designs should be developed to minimize plugging problems and to allow for cleaning or redeveloping of the delivery system.
- o <u>Fluid Recovery Systems</u>. Equally important to effective delivery of the soil-washing solution to the contaminated interval is recovery of the soil-washing solution and the mobilized oil. Recovery systems can include drainlines, wells, or trenches. Again, the most effective system will be a function of site-specific conditions. Selection of pumps for the recovery systems should include recognition of a need to minimize mechanical emulsion of produced fluids and to handle a wide range of potential flow rates.
- o <u>Produced Fluids Treatment</u>. Fluids produced from in situ soil washing will need to be treated to a point where they can be reused or discharged without detrimental environmental impacts. Since these fluids are likely to contain emulsified oils, their treatment may comprise a major component of the soil-washing remediation effort.

Steps to Implementation

Due to the limited field experiences with in situ soil-washing systems, applications will probably require a relatively high level of preliminary evaluations. Where the potential reduction of residual contamination justifies consideration of in situ soil washing, the following factors should be considered.

Attempts to develop generic surfactant-based soil-washing solutions, both for petroleum and environmental applications, have demonstrated that the types of systems that are successful are a function of site-specific conditions, such as the composition of the porous media, the quality of the water
that is present, and the composition of the oils. For surfactant-based systems, evaluation of effective soil-washing solutions should begin with laboratory evaluations that use site-specific materials.

The types and concentrations of surfactants and viscosity modifiers should be optimized with respect to the following parameters:

- EOR--Interfacial tension and core-flood studies can be run to select a system that is effective in removing a maximum amount of residual oil at the minimum reagent concentrations and cost.
- Treatability Studies--Once a soil-washing solution is selected, laboratory treatability tests should be conducted to evaluate treatment/management strategies and cost for produced fluids.
- Formation Plugging--During core floods, evaluation of soil-washing solutions should include monitoring of pressure drops across the cores through time to identify potential plugging problems due to inorganic precipitation, formation of stable emulsions within the core flood, and/or biological activity.
- Inorganic Leaching--The potential for leaching of inorganics can be evaluated by analyzing column effluent or by conducting shaker-flask leaching studies, using the proposed soil-washing solution and site soils.
- Toxicity--Data regarding the toxicity of the soil washing solution should be obtained.

Upon completion of the laboratory studies, a small-scale field pilot test will probably be appropriate. Emphasis is placed on the word "small" because laboratory data should never be considered an absolute indicator of what will happen in a field application. From a small-scale pilot, the issues discussed for the laboratory studies can be evaluated in the field, and sufficient data can be obtained for evaluation of scaled-up applications.

SUMMARY

Cost-effective remediation of subsurface materials containing waste wood-preserving oils poses a significant challenge. In situ treatment or removal of these wastes is being considered with increasing interest. No "off the shelf" in situ treatment/removal technologies effective in remediating these sites are currently available. In light of this, evaluation

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of means to remediate wood-treating sites requires review and evaluation of innovative technologies. Recent research and field applications have indicated that certain innovative in situ removal techniques may be effective in cleanup of subsurface materials containing waste wood-preserving oil. No single in situ removal or treatment technique is likely to be the most effective technique in all situations. The most cost-effective in situ remediation approach at many sites will likely consist of implementing two or more different techniques in sequence. Generalized ranges of contaminant concentration in which selected in situ removal/treatment techniques will most likely be effective is graphically illustrated in Figure 5. Actual effectiveness and ranges of effectiveness will, of course, depend on project-specific considerations.

The most widely demonstrated and cost-effective of these in situ removal techniques is waterflooding. Waterfloods, when applied with the concept of managing the flow path along which the oil migrates, can be highly effective in recovering the mobile free-phase oils. This technique was demonstrated by the case study of waterflood recovery presented in the text. A primary benefit of waterflood recovery is the removal of the mobile free-phase oil thereby, inhibiting further migration of free-phase oils into uncontaminated areas. Removal of this mobile free-phase oil using a waterflooding technique will, in almost all circumstances, be the most cost-effective first step in situ remediation.

A shortcoming of waterflooding is that a significant amount of residual oil cannot be recovered. This residual oil can act as a long-term source of dissolved contaminants. Thus, the most promising application of waterfloods may be as an in situ pretreatment step, with more costly in situ treatment/removal techniques following to achieve lower residual contaminant concentrations.

Several innovative in situ soil-flushing techniques appear promising for achieving these lower residual contaminant concentrations. Surfactant flooding seems to have the most potential, and has been studied the most extensively. Surfactant flooding has been effective in bench-scale studies, but little success has been demonstrated in field application. However, it is an innovative technology in environmental applications, and more success may be achieved after further technological development. A key to achieving this success may be more effective technology transfer from the EOR industry.

Currently, waterflooding and other in situ soil-washing techniques cannot be considered proven remediation techniques. In general, development and testing of site-specific applications of these techniques are required before they can be considered at a particular site for remediation of subsurface



IN SITU BIOREMEDIATION

IN SITU SOIL WASHING

WATER FLOOD HYDROCARBON RECOVERY



REMEDIATION TECHNIQUES

materials containing waste wood-preserving oils. These studies can be costly, but may be justified in the absence of cost-effective site cleanup alternatives.

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PHYSICAL SEPARATION FOR EXCAVATED SOILS AND IN-SITU VACUUM EXTRACTION

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EPA R&D PROGRAM ON TREATMENT OF EXCAVATED SOILS, SLUDGES AND SEDIMENTS

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BACKGROUND

The Superfund research and development program that has been conducted at Edison, NJ has, since the inception of Superfund, been focused on the development and demonstration of mobile technologies for cleanup of waste sites. During the middle and late 1970's several prototypical mobile systems were developed by other EPA research programs that were focused on cleanup of spills of oils and hazardous materials, including a mobile incineration system, a mobile soils washing system, a mobile water treatment system and other systems for on-site cleanup. The intention of the development and demonstration of these prototypes has been to influence the private sector to develop similar, better systems based upon the government-sponsored research, and to make those systems available to EPA, the states, and private companies for contract cleanups.

Thus far, the program has been highly successful, particularly with the influence of mobile incineration and mobile water treatment technologies. Now, these technologies are widely available commercially after the first field uses of such systems were undertaken and publicized by EPA.

PROGRAM GOAL

The current thrust of the Superfund R&D being undertaken at Edison, NJ is to influence and encourage commercial development and utilization of viable systems for on-site treatment of soils, sludges, and sediments at Superfund and other remediation sites. In particular, extraction of contaminants using water with or without additives and other extraction fluids in liquid or gaseous states, is being pursued toward achieving volume reduction as a treatment concept.

DEFINITIONS

Volume reduction for excavated materials is a multi-step treatment process that separates the contaminated solids into two fractions: a larger sized fraction consisting of cleaned soils and other solids that have a small enough measurable residual contaminant present that they can be returned to the original excavation or can otherwise be treated as nonhazardous materials, and a smaller sized fraction consisting of concentrated contaminant typically contained in a fluid or sludge. This concentrated contaminant must be subjected to further treatment or disposal techniques for the cleanup to be complete.

PROGRAM DESIGN

The program is divided into five major areas of activity:

- ° Characterization of the problems.
- ^o Evaluation of the current state-of-art.
- Development and demonstration of promising, viable systems.
- ° Technology transfer to EPA client offices and the private sector.
- ° Coordination with other organizations performing similar work.

Characterization of the Problems

Extraction of contaminants from excavated soils, sludges, and sediments is a technology areas that encompasses a wide variety of specific problem types and potential technical approaches. No single system or approach now commercially available or currently under development will successfully separate all known contaminants from all known site situations. Evaluation of the performance of existing technologies and the development of new ones should ideally be accomplished according to a priority scheme that takes into account the technical tractability of problems and their frequency of occurrence. Further, treatability testing protocols are needed to evaluate the expected performance of candidate cleanup technologies. Therefore, it is necessary to analyze these problem types with respect to the general capabilities of available technologies and develop problem characterization approaches.

Three key sets of information needed are the distinction of repetitive situations from unique ones, the distinction of relatively simple situations for relatively complex ones, and the determination of the numbers of sites or volumes of materials that are associated with the most highly repetitive situations, both simple and complex. For example, from a technological viewpoint, highly volatile organics are treatable by different approaches than semi-volatiles or nonvolatiles; metals and inorganics may require different approaches than those used for organics. Combinations of metals and organics may require sequential treatment in ways that are more complex than if organics alone were present. Radioactive contaminants, a specialized subset of metals contamination, may require treatment techniques related to those used for metals but having certain unique characteristics.

Once these sets of information are developed and organized, and using information regarding the current commercial state-of-the-art, priority decisions can be made regarding expenditure of funds for the purpose of developing technologies. Such developments are most likely to succeed if aimed first at the highest frequency of occurrence, simplest to solve problems, and secondarily aimed at problems having either greater complexity or lower frequencies of occurrence or both.

One characterization scheme is to divide sites up by the industries that contributed the wastes. This approach is particularly useful for single industry sites such as underground storage tanks for fuels, wood treating sites, lead battery reclaimer sites, and sites having radioactive contamination from various man made sources. Some data on sites of these types are available through OERR.

An alternate characterization approach is to group sites according to the type of contaminant present (e.g., organics, metals, radioactive) or the nature of the soils (e.g., relative percentages of sands, silts, clays, and humic materials).

A major activity related to characterization has been the development of standard soils matrices ("SSM") for use in comparing the performance of soils treatment technologies at bench- and pilot-scales. These matrices consist of reproducible blends of specially selected soils and chemicals to simulate Superfund site soils. The matrices are currently in use in support of the SITE program to assist in demonstrations of new soils treatment systems.

Example projects currently ongoing or planned in this technology area include:

- [°] Development of standardized soil and contaminant combinations for evaluating soils treatment systems.
- ^o Development of a mobile soils treatability laboratory.
- Development of treatability testing protocols for contaminant extraction technologies for soils.

Evaluation of the Current State-of-the-Art

In order to advance the state-of-the-art, it is obviously necessary to understand the capabilities of existing technologies, available in the U.S. and internationally. We must be aware of technologies that are currently available fur use at waste sites as well as those available through related industries, such as the chemical process, food and mining industries. Further, as new techniques are developed commercially, it is necessary to evaluate their performance for the specific situations for which they were designed, and to obtain objective performance data of known quality. The program has developed state-of-the-art studies, and will take advantage of the SITE program at full-scale and at pilot-scale to provide needed data. Further, the program will support treatability studies jointly with OSWER to obtain needed performance data for site-specific problems.

Example projects currently ongoing or planned in this technology area include:

- Report: "Technological Approaches to Cleanup of Radiologically Contaminated Superfund Sites".
- Interim Draft Report: "Assessment of Technologies for the Remediation of Radioactively Contaminated Superfund Sites".
- ^o Draft Report: "Cleaning Contaminated Excavated Soil Using Extraction Agents".
- Participation in OSWER's "Engineering Forum" for treatability studies on site-specific problems.
- Participation in the SITE program relative to evaluation of commercial full-scale and pilot-scale (Emerging Program) systems.

Development and Demonstration of Promising, Viable Systems

Once the problem types are understood, and the existing commercial technologies are understood, a development and demonstration program can be designed. The development and demonstration portions of the program are intended to identify and develop new, viable approaches at bench- and pilot-scales and to demonstrate the pilot-scale systems at Superfund sites. Included in the program are technologies to control dusts and vapors from excavations, and techniques to handle debris and other feed problems.

A mobile treatability system is being constructed as the overall goal of the program area on "Development and Demonstration". This capability will consist of a mobile laboratory in which to perform bench-scale studies and other support of on-site treatability tests, and a set of interconnected semi-trailers on which will be mounted pilot-scale versions of numerous soils washing systems. When complete, the mobile system will be useable for pilotscale testing at Superfund sites to assist in resolving site-specific problems.

Example projects currently ongoing or planned in this technology area include:

- ° Control of dusts and vapors released during excavation.
- Treatment of recovered vapors with encapsulating foams.
- Identification of feedstock preparation and debris handling technologies.
- [°] Identification of interrelationships between contaminants and soil particles.
- Development of a sequenced batch reactor for microbial mineralization of excavated soils.
- Development of vacuum-assisted steam stripping system for treatment of excavated soils.
- Development of a pilot system for extraction of semi-volatile organics using ultrasonic contacting.
- Development of a pilot system for extraction of lead and other heavy metals from excavated soils.

- Preparation of a pilot-scale trommel washer system for particle size separation/volume reduction treatment of excavated soils.
- Development of a sonic-frequency extraction system for semivolatile contaminants on excavated soils.

Technology Transfer to EPA Client Offices and the Private Sector

Given the stated program goal of influencing the private sector to utilize promising technologies on tractable problems, the transfer of information developed under this program at public expense takes a high priority. There are four activities ongoing within this program area to accomplish technology transfer: Use of the Federal Technology Transfer Act (FTTA); conducting technical support efforts for regional site-specific problems, developing and maintaining information exchange systems, and conducting information exchange meetings.

Under the FTTA, a soils washing system previously developed by ORD will be transferred for use by a private company interested in using the system for site cleanup activities. The system consists of a trommel washer and a froth flotation cell modified into a four cell countercurrent chemical extractor. Additional efforts will likely be conducted in the future to utilize this broad-based FTTA authority to enhance information interchange between EPA and companies interested in using advanced technologies for site cleanups.

As noted above, technical support efforts are conducted to help solve site specific Regional needs, predominantly in the form of participation in the "Engineering Forum". Many of these efforts have involved laboratory scale treatability studies to determine the potential performance of particle size separation for volume reduction. Future efforts will include use of the mobile pilot-scale soils treatment system for on-site treatability studies.

Additional technical support efforts include a Technical Information Exchange to provide printed and computerized information regarding ongoing programs and technologies at Edison, NJ.

A seminar on extraction of contaminants from excavated soils was held in Edison, NJ with vendors and other interested parties in early December, 1988 and with a synopsis of that meeting will be made available by Summer, 1989.

Coordination With Other Organizations Performing Similar Work

This program area does not have currently defined projects, however, as treatment of excavated soils becomes a more accepted technology and as a greater number of vendors become interested in providing hardware or services, a greater number of organizations will become interested in the technology area. To be successful, our program must maintain coordination with those organizations to avoid duplication of effort and to encourage information exchange.

For more information about the program in general or the status of specific projects, contact Richard Traver, Program Manager, at FTS 340-6677 or (201) 321-6677. For information regarding radiological problems, contact Darlene Williams at FTS 340-6925 or (201) 906-6925. For information regarding the Technical Information Exchange and the associated Computerized On-Line Information System (COLIS), contact Hugh Masters at FTS 340-6678 or (201) 321-6678. For information regarding SITE projects pertaining to extractive technologies, contact Mary Stinson at FTS 340-6683 or (201) 321-6683.

GROUNDWATER CONTAMINANTS AT WOOD TREATMENT FACILITIES

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GROUND-WATER CONTAMINANTS AT WOOD TREATMENT FACILITIES

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Ground-water contamination at five wood treatment facilities across the country have been compared. The distributions of organic priority pollutants at the five sites are similar with the most common contaminants being polynuclear aromatic hydrocarbons and phenolic compounds. These contaminants are the predominant constituents of creosote and their relative concentrations in ground water are controlled by solubility, adsorption, and biodegradation. The distributions of the organic priority pollutants at the five sites are different than those at an "average" hazardous waste site and specific recommendations for monitoring wood treatment facilities will be made. Inorganic contaminants have also been detected at these sites, but their distributions are not uniform across all the sites. Jeffrey K. Rosenfeld and Russell H. Plumb Jr., Lockheed Engineering & Sciences Company, Las Vegas, Nevada 89119.

ABSTRACT

Ground-water contamination at five wood treatment facilities across the country has been compared. The distributions of organic priority pollutants at the five sites are similar, with the most common contaminants being polynuclear aromatic hydrocarbons and phenolic compounds. These contaminants are the predominant constituents of creosote and their observed concentrations in ground water appear to be controlled by solubility, adsorption, and biodegradation. The distributions of the organic priority pollutants at the five sites are different than those at an "average" hazardous waste site and specific recommendations for monitoring wood treatment facilities are made. Inorganic contaminants have also been detected at these sites, but their distributions are not uniform across all sites.

INTRODUCTION

Ground-water contamination at wood treatment facilities is a serious environmental problem with over 40 wood sites currently on the U.S. Environmental Protection Agency National Priorities ("Superfund") List. In addition, as a result of the permitting requirements of the Resource Conservation and Recovery Act, groundwater monitoring is occurring at numerous other wood treatment sites. The purpose of this study is to characterize the groundwater contamination at several of these sites in order to determine if there is a consistent "chemical fingerprint" for the wood treatment industry. In this way, a set of ground-water monitoring parameters can be customized for the industry and this fingerprint could potentially be used to pinpoint the source of contamination identified during a regional investigation.

This study used ground-water data from five wood treatment sites across the country. These sites are located in Arkansas, Georgia, Idaho, Mississippi, and Texas. They were chosen because of the availability of complete ground-water chemical data including organic priority pollutants, metals, and water quality measurements. The facilities appear to have used creosote as the primary wood preservative, but pentachlorophenol and metal arsenate were also used. The distribution of chemicals detected in the ground water at these sites and their average concentration are discussed below. In addition, a suggested approach for monitoring wood treatment facilities, based on the findings of this study, is presented at the end of the paper.

RESULTS

Organic Constituents

The results for the 126 Target Compound List compounds are shown in Figures 1 through 4. The Target Compound List (Table 1) is the list of organic compounds specified by the EPA in the Contract Laboratory Program and includes the volatiles, semivolatiles, PCBs, and pesticides normally analyzed by EPA methods 624, 625, and 608. The top graph in each of the figures shows the percentage of samples in which the compound was detected at each site and the lower graph shows the average concentration. The frequency of detection for each compound is generally less than 50% at each of the sites, because at least half of the samples taken at each site were taken from non-contaminated wells. The average concentration shown is the mean of the concentrations in the wells where the compound was actually detected. In this way, the average concentration was not affected by the number of clean wells sampled at the site.

The first 34 compounds in the Target Compound List are the volatile organic compounds. Figure 1 summarizes the volatile results at the 5 wood treatment facilities, as well as an industry average for the 5 sites. The first thing to notice is the consistency of the results. If a compound was detected at one site, then most likely it was also found at other sites as well. A large number of the volatile compounds were not detected at any of the sites.

The volatile compounds detected at most of the sites include benzene (#23), toluene (#29), ethylbenzene (#32), and xylene (#34). These are all simple aromatic hydrocarbons commonly detected in fuels. They are most likely present in the ground water, as a result of either being in the low distillation end of the creosote itself, or in the carrier used for the creosote, or possibly as degradation products from the more complex aromatic hydrocarbons found in creosote.

The most commonly detected volatile organic compounds are methylene chloride (#5) and acetone (#6). These are common laboratory contaminants, found not only in the contaminated samples, but also the "clean" samples and the blanks at the different sites.

The lower half of Figure 1 presents the average concentration data for the volatile organic compounds. The major ground-water contaminants, benzene, toluene, ethylbenzene, and xylene, are present in the 5-300 ppb range. The laboratory contaminants, methylene chloride and acetone, have relatively low concentrations (<50 ppb) typical of a laboratory contamination problem.

There are 65 semi-volatile compounds on the Target Compound Figure 2 summarizes the monitoring data for the first 33 List. compounds. The compounds commonly detected at the wood treatment facilities include phenol (#35), 2-methylphenol (#42), 4methylphenol (#44), 2,4-dimethylphenol (#50), naphthalene (#55), 2-methylnaphthalene (#59), and acenaphthylene (#66). The first four are phenolic compounds and the last three are polynuclear aromatic hydrocarbons (PAH). These two compound types are the predominant constituents of creosote. Creosote is a very complex mixture of organic compounds whose exact composition depends on the coal tar from which it is produced. It generally contains about 85% PAH and from 2-17% phenolic compounds (Ehrlich, et al., 1982). PAH and phenolic compounds, with the exception of The acenaphthylene, are not only commonly present, but also occur at fairly high concentrations ranging from 500-11,000 ppb.

Figure 3 shows the frequency of detection data for the remaining half of the 65 semi-volatile compounds. The commonly occurring compounds include the following PAH compounds: acenaphthene (#69), fluorene (#76), phenanthrene (#83), anthracene (#84), fluoranthene (#86), pyrene (#87), benz(a)anthracene (#90), chrysene(#91), benzo(b)fluoranthene (#94), benzo(k)fluoranthene (#95), benzo(a)pyrene (#96) and indeno(123-cd)pyrene (#97). These are again fairly common constituents of creosote.

Other semi-volatiles commonly detected include dibenzofuran (#72), which is a constituent of creosote, and bis(2-ethylhexyl) phthalate (#92), which is a laboratory contaminant commonly found in blanks, clean, and contaminated samples. A surprising result was the lack of pentachlorophenol (PCP-#82) contamination. Most likely, this is because these sites have predominantly used creosote for preservation rather than PCP. The Texas facility had used PCP, but discontinued its use in 1962. It may be that PCP was never in the ground water at the Texas site or if it was, the PCP has been biodegraded in the 25+ years since its use. PCP can be a major ground-water contaminant. Ground-water concentrations from a PCP site (not included in this study because of only partial analytical results) ranged from 1 ppb to more than 100 ppm.

The average concentrations for the semi-volatile compounds in Figure 3 are lower than for the first group of semi-volatiles (Figure 2), but are still generally in the 200-5,000 ppb range.

Pesticides and PCBs were generally not detected in the ground water beneath the five wood treatment sites (Figure 4). The peak at #125 is from one sample at one site containing 3 ppb of PCB-1254. The lack of pesticide contamination was somewhat surprising in view of the amount of wood that was stored at these sites. It suggests that additional pesticides, other than creosote, may not have been used for pest control at the sites. In summary, only 27 of the 126 Target Compound List compounds were commonly detected in the ground water at the 5 wood treatment sites. Six were volatile compounds and the other 21 semivolatiles. Of the total, three compounds were most likely the result of laboratory contamination rather than wood preserving. The remarkable thing about these results is the consistency of compound detection. If a compound was present at one site, then it was most likely present at several of the other sites. The ground-water monitoring results suggest a fairly strong industryspecific chemical fingerprint, due to the consistent detection of the commonly occurring compounds and the large number of Target Compound List compounds that were not detected at the sites.

The organic constituents results are summarized in Tables 2 Table 2 shows the industry average for the 25 most common and 3. compounds ranked by frequency of detection. The polynuclear aromatic hydrocarbons are the predominant compound type in the ground water. The PAH compounds are shown with their carbon number - the higher the carbon number, the more complex the compound. For example, naphthalene at C10 is made up of two fused benzene rings, while benzo(a)pyrene at C20 has 5 fused benzene rings. More importantly, the solubility of the PAH compounds decrease with increasing carbon number. Naphthalene, with a solubility of 34 mg/l, is nearly 10,000 times more soluble than benzo(a)pyrene. In addition, the higher carbon number PAH compounds are more strongly adsorbed onto the organic carbon in soils than the less complex PAH compounds. Benzo(a) pyrene is over 500 times more strongly adsorbed than naphthalene from a comparison of their octanol/water partition coefficients (Ekambaram, 1986).

The frequency of detection data show that the smaller carbon number PAH compounds are more commonly detected in ground water than the more complex ones. This makes sense in that they are more soluble and less strongly adsorbed, and therefore more mobile. The two volatile laboratory contaminants, acetone and methylene chloride, are the two most commonly detected compounds. The volatile aromatic compounds, benzene, toluene, ethylbenzene, and xylene are also among the top 25 compounds.

Table 3 shows the industry average ranked by average concentration. Four of the six compounds with the highest average concentration are phenolic compounds. This can be explained by their much higher solubilities compared to the PAH compounds, despite their much lower concentrations in creosote. For example, naphthalene, the most soluble PAH and the most common constituent in creosote, is approximately 2000 times less soluble than phenol. The PAH compounds generally show decreasing average concentration with increasing carbon number. This is in keeping with the more complex PAH compounds being less mobile (lower solubility and higher adsorption) and also being less abundant in creosote than the simpler ones. A sample at the Idaho site supplied additional information on the issue of mobility of the different chemicals in creosote. Creosote was encountered in the saturated zone while drilling, and a sample was taken of the creosote-contaminated water which seeped into the borehole. Table 4 shows the comparison of the chemical composition of the creosote-contaminated water and the ground water at the site.

The major constituents are PAH compounds and phenols with some concentrations in excess of one million ppb. These are the major components of creosote and these levels are above the solubility of these compounds suggesting more of a water/creosote mixture, rather than only a water sample. Naphthalene is the most abundant chemical present in the waste sample, which is consistent with it being the most abundant chemical in creosote and the most soluble PAH. The concentrations of the PAH compounds generally decrease with increasing carbon number, which agrees with the composition of creosote, the decreased solubility, and the increased adsorption of the more complex PAH compounds.

Table 4 also contains the average ground water concentrations at the Idaho site in order to compare the relative mobility of the different chemicals. The chemicals detected in ground water more or less follow the same concentration trend as seen in the waste sample. This suggests that the predominant control on the concentration is the chemistry of the source material. However, the ratio of the concentrations in the waste sample and the average ground water suggest that there are other controls on mobility. The ratios for the PAH compounds range from about 2,000 for naphthalene (C10) to almost 19,000 for benzo(a)pyrene (C20). This agrees with the general trend that the more complex PAH compounds are not as mobile as the simpler ones. The phenols, which are all more soluble than the PAH compounds, have lower ratios which suggest that they are more mobile.

Mobility is controlled not only by solubility and adsorption, but also by chemical reaction and biodegradation, which can result in either the destruction or production of certain chemicals. The production of simpler PAH compounds is suggested by this Idaho sample, in which anthracene, acenaphthylene, and fluorene were not detected in the waste sample (granted at a high detection limit), but were detected in the ground water.

Inorganic Constituents

Ground water samples at the sites were also analyzed for metals and other inorganic constituents. The inorganic results were compared in order to determine if there was a consistent inorganic fingerprint at the sites, as was observed for the organic priority pollutants. Possible metals to consider include arsenic, chromium, and copper, because of the use of chromated copper arsenate as a wood preserver. Inorganic contamination must be dealt with differently than organic contamination, because the inorganics are commonly naturally occurring. Therefore, background values must be determined and compared with the sample results. In this study, the wells which did not show any organic contamination were chosen to be the background wells and compared with the wells which did show organic contamination.

Inorganic constituents, in which the ratio of the average contaminated concentration for the site to the background concentration was greater than 3, were used as indicators of contamination. The value of 3 (or a 300% increase in concentration) was chosen arbitrarily, in order to reduce some of the noise created by using total metal concentrations rather than dissolved concentrations. Each site seemed to have a number of samples (both contaminated and clean), in which all the concentrations (especially iron, lead and aluminum) are much higher than for the other samples. These values are most likely the result of samples containing high concentrations of suspended material, rather than inorganic indicators of contamination.

Figure 5 shows the number of sites at which individual parameters exceeded the contaminated/clean ratio of 3. Of the thirteen parameters shown, only manganese suggests any indication of contamination at more than three sites. Therefore, unlike the organic results, there do not appear to be any clear inorganic indicators of contamination for wood treatment facilities. The increased concentration of manganese is not easily explained, since manganese does not appear to be used in the wood preserving Manganese is more soluble under reducing conditions process. (Stumm and Morgan, 1970), and the increase in concentration may be a consequence of the ground water becoming anoxic due to the abundant organic contamination. It was surprising that arsenic, chromium, and copper did not show up more often, but this may be due to the fact that these facilities used predominantly creosote in their operations.

Comparison with "average" hazardous waste site

Previous studies at EMSL-Las Vegas have examined the distribution of organic priority pollutants at over 100 hazardous waste sites (Plumb and Pitchford, 1985). These studies have pointed out the importance of monitoring for volatile organic compounds and showed that they accounted for over 75% of the organic compounds detected at hazardous waste sites. It was also shown that the number of volatile compounds detected could be correlated with the number of priority pollutants detected and that by measuring only the volatiles, one could predict the number of priority pollutants that would be detected at a site. The wood treatment facilities appear to differ from most hazardous waste sites, because of the nature of the chemicals used for wood preserving. Creosote consists predominantly of semivolatile polynuclear aromatic hydrocarbons and phenolic compounds. These semi-volatile compounds were also the principal ground-water contaminants detected at the wood treatment sites. Therefore, the approach of just monitoring for volatile compounds, in order to predict the need for more extensive characterization of the groundwater samples, would not really work at these facilities.

Figures 6 through 9 show the Target Compound List compounds detected at the average hazardous waste site compared to the industry average for these 5 wood treatment facilities. The volatiles (Figure 6) show a wider variety of compounds detected at the hazardous waste sites compared to the wood sites. The predominant volatile compounds at the average hazardous waste site include the chlorinated compounds, such as trichloroethene, perchloroethene, and dichloroethene. These compounds were not detected at the wood sites. The semi-volatile compounds (Figures 7 & 8) are relatively unimportant at the average hazardous waste However, as shown previously, they are the predominant site. ground-water contaminants at the wood sites. Pesticides (Figure 9) have been observed to be more abundant at the average hazardous waste site than at the wood treatment facilities.

SUMMARY

In summary, this study has demonstrated the predominance and consistency of semi-volatile organic contamination of ground water at creosote wood treatment facilities. It must be stressed that the study dealt mainly with creosote facilities. If data had instead been received from a group of arsenate facilities, this study would have had a different emphasis. So in developing a monitoring strategy for a wood facility, it is important to know what process the facility used.

In terms of monitoring parameters for wood treatment facilities, the semi-volatile compounds should be emphasized. This should be effective for both creosote and PCP facilities. If the facility used an arsenate process, then metals analyses should be routinely incorporated into the monitoring program. During an initial site investigation, at least some of the samples should be analyzed for all priority pollutants and metals, because of the possibility of multiple wood treatment processes at the same site. Monitoring results for volatile compounds could be important, because these compounds are more mobile than the semi-volatiles and could be in a separate plume. One of the surprises of this study is that the volatiles and semi-volatiles occurred in the same wells and were not separated by their different mobilities.

Teflon or stainless steel well casing are recommended for site investigations at wood treatment facilities. PVC should not be used, because of the possibility that it could interact with and/or be degraded by the organic compounds. Since the semi-volatiles are the predominant type of organic compound present, the type of sampler used is not as critical as if the contamination at wood treatment facilities were predominantly volatile compounds. Sampling at the top of the water table to collect both water and floaters is recommended. PCP is used with a solvent and is commonly found with the floaters. Creosote, on the other hand, is a sinker and therefore, sampling at the bottom of the aquifer may also be necessary.

Since the polynuclear aromatic hydrocarbons are strongly adsorbed onto the soil and not volatile, collecting soil samples and sending them to the laboratory for semi-volatile analysis is recommended for determining extent of soil contamination, rather than attempting a soil gas survey.

ACKNOWLEDGMENT

This work was conducted under Task Directives 4DM02 and 89G01 of Contract 68-03-3245 between the U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Las Vegas, Nevada, and Lockheed Engineering & Sciences Company, Las Vegas, Nevada. The EPA Technical Monitor is Steven P. Gardner.

NOTICE

Although the research described in this document has been funded wholly or in part by the United States Environmental Protection Agency, it has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

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Figure 1. Frequency of detection and average concentration for volatile organic compounds at wood treatment facilities.







Figure 3. Frequency of detection and average concentration for semi-volatile organic compounds at wood treatment facilities.



Figure 4. Frequency of detection and average concentration for pesticides and PCBs at wood treatment facilities.



Figure 5. Inorganic monitoring parameters with contaminated/clean concentration ratios greater than 3.



Figure 6. Frequency of detection for volatile organic compounds at an "average" wood treatment facility and hazardous waste site.



Figure 7. Frequency of detection for semi-volatile organic compounds at an "average" wood treatment facility and hazardous waste site.



Figure 8. Frequency of detection for semi-volatile organic compounds at an "average" wood treatment facility and hazardous waste site.



Figure 9. Frequency of detection for pesticides and PCBs at an "average" wood treatment facility and hazardous waste site.

TABLE 1. TARGET COMPOUND LIST

NUMBER	CHEMICAL NAME	NUMBER	CHEMICAL NAME	
	CHIODOMETHANE		2-NITROANII INF	
2	BRONOMETHANE	65	DIMETHYL PHTHALATE	
3	VINYL CHLORIDE	66	ACENAPHTHYLENE	
4	CHLOROETHANE	67.	2.6-DINITROTOLUENE	
5	METHYLENE CHLORIDE	68	3-NITROANILINE	
6	ACETONE	69	ACENAPHTHENE	
7	CARBON DISULFIDE	70	2,4-DINITROPHENOL	
8	1,1-DICHLOROETHENE	71	4-NITROPHENOL	
9	1,1-DICHLOROETHANE	72	DIBENZOFURAN	
10	1,2-DICHLOROETHENE	73	2,4-DINITROTOLUENE	
11		74	VIEINIL PHINALAIC	
12	2. BUTANONE	76	FILMDENE	
14	1 1 1-TRICHLOROFTHANE	77	4-NITROANIE INF	
15	CARBON TETRACHLORIDE	78	4.6-DINITRO-2-METHYLPHENOL	
16	VINYL ACETATE	79	N-NITROSOD LPHENYLAMINE	
17	BROMOD I CHLOROMETHANE	80	4-BROMOPHENYL PHENYL ETHER	
18	1,2-DICHLOROPROPANE	81	HEXACHLOROBENZENE	
19	CIS, 1, 3-DICHLOROPROPENE	82	PENTACHLOROPHENOL	
20	TRICHLOROETHENE	83	PHENANTHRENE	
21	CHLOROD I BROMOMETHANE	84	ANTHRACENE	
22	1,1,2-TRICHLOROETHANE	85	DI-N-BUTYL PHTHALATE	
23	BENZENE	00 97	PLUCKANTHENE	
24	TRANS-1, 3-DICHLOROPROPENE	0/ 33	PIKENE Dutvi dentvi dutnai ate	
25		80	3 31-DICHLORODENZIDINE	
20	4 THE INIL C PENIANUNE	07	DENT/ANANTHDACENE	
27		90		
20	TOULIENE	92	RIS(2-FTHYLNEXYL) PHTHALATE	
30	1.1.2.2-TETRACHI OROFTHANE	93	DI-N-OCTYL PHTHALATE	
31	CHLOROBENZENE	94	BENZO(B)FLUORANTHENE	
32	ETHYLBENZENE	95	BENZO(K)FLUORANTHENE	
33	STYRENE	96	BENZO(A)PYRENE	
34	XYLENE, TOTAL	97	INDENO(1,2,3,-CD)PYRENE	
35	PHENOL	98	DIBENZ(A, H)ANTHRACENE	
36	BIS(2-CHLOROETHYL)ETHER	99	BENZO(GHI)PERYLENE	
37		100	BHU-ALPHA	
30	1,3*DICHLOROBENZENE	101	BRC-CANNA (I INDANE)	
2 7		102	BHC-DELTA	
40		103	NEDTACHI OD	
41	2-METNYI DHENOI	105		
43	RIS(2-CHI OROISOPPOPYI) ETHER	106	HEPTACHIOR FRONTOF	
44	4-METHYLPHENOL	107	ENDOSULFAN 1 (ALPHA)	
45	N-NITROSODI-N-PROPYLAMINE	108	DIELDRIN	
46	HEXACHLOROETHANE	109	4,4'-DDE	
47	NITROBENZENE	110	ENDRIN	
48	ISOPHORONE	111	ENDOSULFAN 2 (BETA)	
49	2-NITROPHENOL	112	4,4000	
50	2,4-DIMETHYLPKENOL	113	ENDOSULFAN SULFATE	
51	BENZOIC ACID	114	DDT-P,P' (4,4'-DDT)	
52	BIS(2-CHLOROETHOXY) METHANE	115	METHOXYCHLOR	
55		110	ENDRIN KETUNE	
74 65	I, C, 4 - IKI URLUKUBENZENE NADUTUAI ENE	11/	CHLORDANE SETA	
37 54	A-CHIOPOANII INF	110	TOYADHENS	
57	HEXACHLOROBUTADIENE	120	PCR-1016 (AROCLOR 1016)	
58	4-CHLORO-N-CRESOL	121	PCB-1221 (AROCLOR 1221)	
59	2-METHYLNAPHTHALENE	122	PC8-1232 (AROCLOR 1232)	
60	HEXACHLOROCYCLOPENTAD IENE	123	PCB-1242 (AROCLOR 1242)	
61	2,4,6-TRICHLOROPHENOL	124	PCB-1248 (AROCLOR 1248)	
62	2,4,5-TRICHLOROPHENOL	125	PCB-1254 (AROCLOR 1254)	
63	2-CHLORONAPHTHALENE	126	PCB-1260 (AROCLOR 1260)	

			PERCENT	AVERAGE	# OF
	COMPOUND NAME	PAH	DETECT	CONCENTRATION	SITES
	арание Хортоме		 109		A
2	METHVIENE CHIODIDE		423	20	4
2	ACENA DHTHENE	C12	420	24	4
4	NA DHTHA LENE	C10	358	3313	5
5	FIJORENE	C13	348	5512	5
6	RIS(2-ETHYLHEXVL) PHTHALATE	613	328	14	ך אריי
7	PHENANTHRENE	C14	298	1825	5
8	DIBENZOFURAN	U 11	28%	332	<u>ح</u>
9	2-METHYLNAPHTHALENE	C11	27%	563	4
10	BENZENE		228	33	4
11	FLUORANTHENE	C16	228	1028	4
12	PYRENE	C16	228	666	4
13	ANTHRACENE	C14	218	425	4
14	TOLUENE		20%	48	4
15	ETHYLBENZENE		198	39	4
16	XYLENE, TOTAL		18%	94	4
17	2,4-DIMETHYLPHENOL		138	1219	3
18	BENZ (A) ANTHRACENE	C18	138	280	4
19	CHRYSENE	C18	138	249	4
20	ACENAPHTHYLENE	C12	138	59	4
21	2-METHYLPHENOL		128	1268	3
22	PHENOL		12%	1537	3
23	4-METHYLPHENOL		11%	3640	3
24	BENZO (B) FLUORANTHENE	C20	88	121	3
25	BENZO (A) PYRENE	C20	88	57	3

TABLE 2. WOOD TREATMENT INDUSTRY AVERAGE (5 SITES) - BY PERCENT DETECT
TABLE 3. WOOD TREATMENT INDUSTRY AVERAGE (5 SITES) - BY AVERAGE CONCENTRATION

			PERCENT	AVERAGE	# OF
	COMPOUND NAME	РАН	DETECT	CONCENTRATION	SITES
1	4-METHYLPHENOL			3640	3
2	NAPHTHALENE	C10	35%	3312	5
3	PHENANTHRENE	C14	298	1825	5
4	PHENOL		12%	1537	3
5	2-METHYLPHENOL		128	1268	3
6	2,4-DIMETHYLPHENOL		138	1219	3
7	FLUORANTHENE	C16	228	1028	4
8	ACENAPHTHENE	C12	388	805	5
9	PYRENE	C16	228	666	4
10	FLUORENE	C13	348	661	5
11	2-METHY LNAPHTHALENE	C11	278	563	4
12	ANTHRACENE	C14	218	425	4
13	DIBENZOFURAN		288	332	4
14	BENZ (A) ANTHRACENE	C18	138	280	4
15	CHRYSENE	C18	138	249	4
16	BENZOIC ACID		28	171	1
17	BENZO (B) FLUORANTHENE	C20	88	121	3
18	XYLENE, TOTAL		188	94	4
19	DI-N-OCTYL PHTHALATE		18	60	1
20	ACENAPHTHY LENE	C12	138	59	4
21	BENZO (A) PYRENE	C20	88	57	3
22	TOLUENE		208	48	4
23	ETHYLBENZENE		198	39	4
24	BENZENE		22%	33	4
25	N-NITROSODIPHENYLAMINE		18	22	1

TABLE 4. CONTAMINANTS AT IDAHO SITE

COMPOUND NAME	ран	CREOSOTE WASTE (Ug/L)	AVERAGE GROUND WATER (ug/L)	WASTE/ GROUND WATER
NAPHTHALENE	C10	6,400,000	3251	1,969
PHENANTHRENE	C14	5,000,000	543	9,202
ACENAPHTHENE	C12	2,630,000	871	3,020
FLUORANTHENE	C16	2,140,000	187	11,475
PYRENE	C16	1,730,000	144	12,035
2-METHYLNAPHTHALENE	C11	1,600,000	557	2,875
DIBENZOFURAN		1,180,000	302	3,909
BENZ (A) ANTHRACENE	C18	580,000	34	17,059
CHRYSENE	C18	300,000	21	14,286
BENZO (B+K) FLUORANTHENE	C20	230,000	14	16,429
BENZO (A) PYRENE	C20	170,000	9	18,889
PHENOL		85,000	45	1,889
INDENO (123CD) PYRENE	C22	32,000	3	10,667
2-METHYLPHENOL		25,000	99	253
BENZO (GHI) PERYLENE	C22	22,000	< 1	> 22,000
2,4-DIMETHYLPHENOL		21,000	117	180
ANTHRACENE	C14	< 1000	162	< 6
ACENAPHTHYLENE	C12	< 1000	11	< 91
FLUORENE	C13	< 1000	345	< 3
4-METHYLPHENOL		< 1000	132	< 8

FATE AND TRANSPORT MODELING OF WOOD PRESERVING CONTAMINANTS IN SURFACE WATER Dr. Robert B. Ambrose, EPA-ORD, Athens, Georgia

"Fate and Transport Modeling of Wood Preservative Contaminants in Surface Water"

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- 1. Introduction
 - . Chemicals
 - Pathways
 - . Screening mass balance
 - . Simulation modeling
- 2. Loading to the Stream
 - . Screening calculation
 - . Simulation
- 3. Stream Dilution
 - Screening calculation
 - Spread sheet calculation
 - . Simulation
- 4. Bioconcentration
 - . Screening calculation
 - . Simulation
- 5. Discussion of Results

"Modeling the Transport and Fate of Wood Preserving Wastes in Surface Waters"

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1. Introduction

Uncontrolled wastes from numerous wood preserving facilities pose an unknown risk to aquatic communities and humans. Chemicals associated with creosote, pentachlorophenol, and chromated copper arsenate are allowed to drip from treated wood onto many sites. As chemical concentrations build up in the soil, they threaten ground water through leaching and nearby streams through runoff, erosion, and ground water transport. Driven by the hydrological cycle, these processes are quite variable in time and space. Assessing present and future exposure and risks at a given site requires a combination of site monitoring and modeling. This paper explores the use of simple calculations and more sophisticated simulation models in assessing potential exposure and risk to the aquatic community and to humans through drinking water and eating fish.

Simulations were conducted for pentachlorophenol at hypothetical half acre sites situated 10m and 100m from Heath Creek near Rome, Georgia. The 37 km^2 watershed receives an average of 1347mm of rain per year and yields a stream discharge of 0.76 m³/sec (651mm/yr). Recorded discharge extremes range from 0.034 m³/sec to greater than 20 m³/sec. Soil properties at the site were assumed to reflect local Conasauga soils. Average grade was assumed to be 2%.

2. Screening Calculations

Risk assessments often begin with simple screening calculations to assess whether exposure concentrations are expected to be much greater or much less than aquatic criteria, drinking water standards, or fish tissue standards. These calculations usually employ quite conservative assumptions about the exposure scenario. The resulting margin of safety, however, is usually uncertain, and can be resolved only by more detailed monitoring and more sophisticated modeling.

The screening calculations for stream concentration assume that all chemicals dripping from the wood reach the stream unattenuated:

 $\overline{C}_{w} = L_{D} V_{L} / \overline{Q} \cdot 86400 \cdot 365$ (1) where C_{w} = average stream concentration, mg/L L_{D} = average drippage from lumber, g/m³ V_{L} = volume of lumber treated, m³/yr \overline{Q} = average stream flow, m³/sec

 \overline{C}_w may be directly compared to drinking water criteria, because cancer risk is a long term average process. Aquatic toxicity, however, is a short term event. Usually a low flow with a specified return interval will be used in Equation 1 to obtain the relevant stream concentration.

Screening calculations for whole fish concentration assume equilibrium between fish tissues and the average water concentration:

$$\overline{C}_{F} = \overline{C}_{w} K_{ow} f_{L}$$

where

 $\overline{C_r}$ - average whole fish concentration, ug/g K_{ow} = octanol-water partition coefficient, L_w/L_{oct} f_L = fraction lipid content of fish

These calculations account for bioconcentration to lipid, but not to other tissues. They ignore potential food chain bioaccumulation, which can be important for chemicals with log K_{ow} greater than 5.

For the hypothetical Heath Creek site, the lumber drippage was taken to be 4.36g PCP/m³. Combined with the treatment volume of 2.55 x 10^4 m³/year. the average loading of PCP to the site is 304 g/day. Dividing by the average flow of 0.73 m^3 /sec, the average stream concentration is calculated to be 4.6 ug/L. Given the log K_{ne} of 5 and trout with a lipid content of 0.1, the bioconcentration factor is 10⁴, and the average whole fish concentration is calculated to be 46 ug/g. Little bioaccumulation is expected.

Several potential errors are present in these screening calculations. First, not all the PCP drippage to the site should be expected to reach the stream. Much of it may leach to ground water and never intercept the stream. Second, PCP loadings to the stream via runoff and erosion will be highly irregular, as will the daily stream flows. The average of daily concentrations can be quite different from the volume-weighted average used in the screening calculation. Third, high PCP concentrations during runoff events may sorb to the benthic sediments. Desorption during subsequent days may cause chronic low level contamination and raise average downstream fish concentrations. Fourth, the extent of fish uptake and accumulation may be affected by chemical speciation, unsteady loading, food chain bioaccumulation, and metabolism. The significance of these calculated errors may be explored using a series of simulation models that account for many of the appropriate processes.

3. Models and Methods

The processes simulated in this study are illustrated in Figure 1. The drippage load to the site was assumed to be a steady 304 g/day, as calculated in the screening exercise. Daily runoff, erosion, and leaching fluxes were simulated with the Pesticide Root Zone Model PRZM (Carsel et. al., 1985). PRZM is based on the SCS curve number approach to hydrology, with transport, partitioning, and degradation equations describing chemical fate.

Daily stream concentrations were calculated with simple dilution equations implemented on spreadsheet:

$$C_{1i} = (L_{Ri} + L_{Ei})/Q_i$$
 (3)

$$C_{2i} = \overline{L_i} / Q_i$$
(4)

$$C_{2i} = C_{1i} + C_{2i}$$
(5)

$$C_{3i} = C_{1i} + C_{2i}$$
(5)

where

L_{Ri} = daily runoff loads, g/day L_{Ei} = daily erosion loads, g/day L
_ = average leaching load, g/day Q_i = daily stream flow, m³/day C_{1i} = daily stream concentrations from site receiving runoff and erosion loads, mg/L C_{2i} = daily stream concentrations from leaching only, mg/L C_{3i} = daily stream concentratons from site receiving runoff, erosion, and leaching loads, mg/L

Sorption and desorption were added as a first order attenuation process following runoff events.

Daily whole fish concentrations were simulated with the FGETS model (Barber et. al., 1988). FGETS is a toxicokinetic model that simulates the bioaccumulation of nonpolar organic chemicals by fish from both water and tainted food. Both of these routes of exchange are modeled as diffusion processes that depend upon physico-chemical properties of the pollutant and morphological/physiological characteristics of the fish. Two sets of simulations were run. The first considered bioconcentration from water to trout. The second included bioconcentration to sculpin and bioaccumulation in trout eating sculpin.

4. Chemical Loading Simulations

PRZM was used to simulate daily runoff, erosion, and leaching fluxes from sites that should be typical near Heath Creek. The principal hydrologic parameters determining runoff and erosion are the curve number, precipitation, and soil moisture. Daily meteorological data from NOAA climatological station #7610 (Weather Bureau at the Rome, Georgia airport) were applied to this site for the years 1950 to 1986. Soil moisture is calcualted daily by the model. The principal site parameters determining erosion and runoff are soil type and soil cover. Minimal vegetative cover was specified for these simulations. Sparsely covered ground on poorly drained Conasauga soils will yield high erosion and runoff fluxes. Average soil properties for three layers are given in Table 1. The representative curve number chosen for this site is 91.

Layer	Depth cm	Sand %	Clay %	Organic %	рН
Surface	10.2	25	15	0.50	4.8
Subsurface	48.3	15	47.5	0.17	4.8
Storage	76.2	15	50	0.10	5.05

Table 1. Heath Creek Soil Data

The principal chemical parameter determining rates of contaminant flux is the partition coefficient. The octanol water partition coefficient K_{ow} of PCP varies with pH because the relative fraction of PCP as phenol and as phenate varies with pH. The sediment water partition coefficient K_d varies with K_{ow} and soil organic content. K_d describes the partitioning of PCP between aqueous and sediment phases only. Treated wood, however, receives PCP dissolved in an oil carrier. This oil is mixed and carried with water leaching or running off the site. A coefficient K_{mow} describing partitioning between the oil-water emulsion and the sediment can be calculated from the K_d , K_{ow} , and the relative volumes of water V_w and oil V_o :

$$K_{sow} = K_d / \left(\frac{V_w}{V_w + V_o} + K_{ow} \frac{V_o}{V_w + V_o} \right)$$
(6)

The resulting partition coefficients are summarized in Table 2.

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Layer	Depth cm	K _{ow} (mg/L _o)/(mg/L _w)	K _d (mg/kgs)(mg/L _w)	K _{sow} (mg/kgs)/mg/L _{ow})
Surface	10.2	59,000	80	0.71
Subsurface	48.3	59,000	27	0.21
Storage	76.2	42,000	12	0.15

Table 2. Heath Creek PCP Partitioning Data

The time series of erosion plus runoff loads are shown in Figure 2 (daily loads are shown averaged by month). Over the entire 18 year simulation, the 304 g/day dripping to the site resulted in average runoff, erosion, and leaching of 63 g/day, 1 g/day, and 231 g/day. The remainder, about 3%, remained in the soil on site.

Runoff and erosion loads were assumed to reach the stream with no loss. In reality, some deposition on the watershed below the site is expected. Deposited chemical would be available to runoff and erosion as well as leaching during subsequent rainfall events.

Leaching loads were assumed to reach ground water and be transported toward the stream. Travel times though silt and sand aquifers can be calculated as follows:

Vc	-	365	K [.] s/R	(7))
D		1 +	V alm	18	•

 $R = 1 + K_p \rho / n$ (8) $\tau = L/V_c$ (9) where

V _c	- velocity of the chemical, m/yr
ĸ	= hydraulic conductivity, m/day
s	- slope
R	 retardation factor
K _ρ	 chemical partition coefficient
ρ	- bulk density of the aquifer, g/cc
n	= porosity, or water content
τ	- travel time, years

L = distance to stream, m

Assumed properties and calculations are summarized in Table 3. Travel times for a site 10m from the stream should range from a half year to 33 years. Travel times calculated for the site 100m from the stream are 5 to 330 years. The long travel times in combination with hydraulic dispersion should result in averaged loads reaching the stream. Only a fraction of the contaminated plume would be expected to intercept the stream. For these calculations, the entire plume from the 10m site was assumed to reach the stream. For the site 100m from the stream, the plume was assumed to miss the stream entirely.

Parameter	Silt Aquifer		Sand Aquifer		
K, m/day	1.5		7.5		
n		0.3	0.45		
ρ, g/cc	1.7		1.5		
K.p.	0.15		0.15		
R	1.85			1.5	
s	0.01	0.001	0.01	0.001	
V _c , m/yr	3.0	0.3	18	1.8	
7, yr (10m)	3.3	33	0.56	5.6	
τ, yr (100m)	33	330	5.6	56	

Table 3. Ground Water Transport

5. Stream Dilution Calculations

Daily stream concentrations subject to runoff, erosion, and leachate, given by equations 3-5, were calculated by spread sheet. The time series of fluxes from PRZM, in kg/ha-day, were first multiplied by $1000 \cdot 0.5/2.5$ to obtain loads in g/day from a half-acre site. Daily flows for Heath Creek, in ft³/sec, were extracted from the USGS gaging record and multiplied by 86400/35.3 to obtain flows in m³/day. Stream flows are shown in Figure 3. The calculated stream concentrations subject to erosion and runoff loads only are illustrated in Figure 4. Cumulative distribution functions are shown in Figures 5 and 6. The mean concentration is 3.3 ug/L, corresponding to the 97th percentile. By contrast, mean erosion and runoff loads divided by the mean flow give an average stream concentration of 1.0 ug/L.

The calculated stream concentrations subject to average leaching only are illustrated in Figure 7. The mean concentration is 19 ug/L. Mean leaching divided by mean flow gives 3.6 ug/L.

A site that contributes runoff, erosion, and steady leachate to Heath Creek should produce a mean concentration of 22 ug/L. This compares to the screening calculation of 4.6 ug/L.

The effect of benthic sorption and desorption subsequent to runoff events was explored. During runoff events, a constant plane source equal to the water concentration was assumed at the benthic surface. The concentration distribution in the bed is given by

$$C_{\rm Bz} / C_{\rm B0} = 1 - {\rm erf} (z/\sqrt{4 E_{\rm R} \Delta t})$$
 (10)

and
$$E_{R} = E_{sw} (1 + K_{p} \rho/n)$$
 (11)

where

 C_{Bz} = concentration in pore water at depth z, mg/L C_{B0} = aqueous concentration at benthic surface, mg/L z = depth below benthic surface, m Δt = elapsed time through event, days E_{sw} = sediment-water diffusion coefficient, m²/day E_{R} = retarded diffusion coefficient, m²/day K_{p} = partition coefficient in bed, (mg/kg)/(mg/L) ρ = bulk density of bed, g/cc n = porosity of the bed, Lw/L

For an E_{sw} of 10^{-3} , K_{ow} of 10^5 , ρ of 1, n of 0.4, and benchic organic fraction of 10^{-2} , the retarded benchic diffusion coefficient will be about $10^{-6} \text{ m}^2/\text{day}$. For events lasting 10^{-1} day, surface water concentrations will be 10 times the daily average. Pore water concentrations are calculated to be a half and a tenth of surface water concentrations at depths of 0.3mm and 0.7mm (designated $z_{0.5}$ and $z_{0.1}$, respectively). Total dissolved plus sorbed benchic concentrations C_{BTz} are given by

$$C_{BTz} = C_{Bz} (1 + K_p \rho/n)$$
 (12)

For this example, total concentrations are about 10^3 times per pore water concentrations.

Following runoff events, desorption from the contaminated bed to the surface water can be described by

$$C_{Bz} = C_{BzO} \exp(-E_R t/z^2)$$
 (13)

where

 C_{BzO} = pore water concentration at depth z at the end of the event, mg/L t = elapsed time following event, days

Desorption half lives from various depths are given by

$$t_{1/2} = 0.693/(E_R/z^2)$$
 (14)

For depths where pore water concentrations begin at a half and a tenth of surface concentrations, the quantity E_R/z^2 is 11.0 and 1.85 and half lives are 0.063 days and 0.37 days. Dividing the bed into two layers, we calculate that the upper layer, containing about 75% of the sorbed mass, desorbs over 99% of its mass by a half day following the event. The lower layer, containing about 25% of the sorbed mass, desorbs about 60% of its mass the first half day, 34% during the next fully day and 5% over a following day.

The mass loading from the lower benchic layer following the event and resulting surface water concentrations can be calculated by

$$M_{\rm Bj} = \frac{E_{\rm R} A}{z_2} \qquad (1 + K_{\rm p} \rho/n) \exp(-E_{\rm R} t/z_2^2) \qquad (15)$$
$$C_{i+i} = M_{\rm Bi}/Q_{i+i} \qquad (16)$$

and $C_{i+j} = M_{Bj}/Q_{i+j}$

where

Z₂ = the depth of layer 2, m
 C_{B20} = inital pore water concentration in layer 2, mg/L
 A = benthic surface area contaminated by event, m²
 j = days following an event occuring at time i

Taking z_2 to be approximately $z_{0.1}$, C_{B20} as 10 x 0.25 C_i , a benthic area of A of 2.5 x 10⁴ m², flow of about 1 m³/sec, and other parameters as defined previously, the water concentrations on days following a runoff event are approximated by

 $C_{i+j} = C_i \exp(-1.85 t_j)$ (17)

Adding this function to the spread sheet, a new time series of water concentrations was calculated. The average stream concentration for the runoff and erosion case increased from 3.3 ug/L to 3.4 ug/L as a result.

6. Fish Bioaccumulation Simulations

FGETS was used to simulate whole fish concentration responding to the concentration time series produced by runoff plus erosion and by leaching alone. Two sets of simulations were run for each concentration time series. The first set considered bioconcentration from water to trout only. The second set considered bioaccumulation in trout eating sculpin equilibrated to average PCP concentrations. One major complication required spread sheet adjustments prior to the fish simulations. PCP ionizes from the neutral phenol to the anionic phenate (designated PCP⁻). With a pK_a of 4.8, most molecules in surface water will be as PCP. Only the neutral molecules exchange across fish tissue. Inside the fish, aqueous PCP in the blood partitions to lipid and ionizes to PCP⁻, which also partitions to lipid. The sequence of reactions is shown in Figure 8. The estimated equilibrium coefficients are based on surface water pH of 7.8 and blood pH of 6.8. The high affinity of PCP for lipid should result in about 10 times more PCP than PCP⁻ accumulating in whole fish. It was concluded, then, that ionization inside fish could be ignored and that water concentrations of PCP must be reduced by a factor of 1000 prior to the FGETS simulations. This was accomplished on the spread sheet.

Because trout live about 10 years, only the first halves of the water concentration time series were used. Trout whole body concentrations responding to runoff and erosion loads and to leachate loads assuming no food chain effects are illustrated in Figures 9 and 10. Mean trout concentrations are 40 ppb and 277 ppb, reflecting a log bioconcentration factor of 1.2 (or 4.2 based upon the neutral PCP water concentration). These same mean fish concentrations would have been obtained by running FGETS with the mean water concentrations.

To investigate potential food chain effects, sculpin were simulated with FGETS, and their mean concentrations fed to trout in a second series of trout simulations. Mean sculpin concentrations were 24 ppb and 190 ppb for runoff plus erosion and leaching, respectively. Both reflect a log bioconcentration factor of 1.0 (or 4.0 based upon the neutral PCP water concentration). Mean trout concentrations rose to 43 ppb and 300 ppb, reflecting a log bioaccumulation factor of 1.25 (or 4.25 based upon the neutral PCP water concentration). This one step food chain added only 8% to the trout concentrations.

A final complication that could not be addressed in this study is the metabolism of PCP within fish. FGETS at present does not contain an equation for this process, and rates for trout are unknown. Because metabolism of PCP in fish can occur, these simulations should be considered upper estimates.

7. Summary

The loading, dilution, and fish calculations are summarized in Table 4. Site 1 is located 100m from Heath Creek, and delivers runoff and erosion loads. Site 2 is located 10m from Heath Creek, and delivers runoff and erosion loads as well as a steady average leaching load. Fish concentrations have been extrapolated to the entire period of record using the bioconcentration and bioaccumulation factors calculated by FGETS.

For site 1, the screening calculation overestimates the load by a factor of 4.8 or 380%. The mean concentration is overestimated, however, by only 35%. The effect of ionization causes the screening calulation to overestimate trout concentrations by a factor of 770. For a similar chemical that does not ionize, the screening calculation would actually have underestimated fish concentrations by 23%. Benthic desorption following events is insignificant.

Calculation	L g/day	Cw ppb	C _F ppb	
Screening	304	4.6	46 x 10 ³	<u> </u>
<u>Site 1 Simulation</u> 1	63	3.3	52	
Add benthic desorption	63	3.4	54	
Add food chain	63	3.4	60	
<u>Site 2 Simulation</u> ²	294	22	350	
Add food chain	294	22	390	

Table 4. Summary of Calculations

¹Daily runoff plus erosion

²Daily runoff, erosion, and mean leaching

Ignoring the one step food chain would cause about a 10% underestimate of trout concentrations.

For site 2, the screening calculation overestimates the load by 3%, but underestimates the mean water concentration by a factor of 4.8. The effect of ionization causes the screening calculation to overestimate trout concentrations by a factor of 120. For a similar chemical that does not ionize, the screening calculation would have underestimated fish concentrations by a factor of 8.5. Ignoring the food chain here would have caused a 10% underestimate of trout concentrations.

The largest sources of uncertainty or errors found in this modeling study are the effects of ionization on uptake, the amount of chemical delivered to the stream from the site, and the effect of daily averaging rather than volume weighted averaging. Food chain effects, not of major importance here, are expected to be significant for longer food chains and slightly more hydrophobic chemicals. Further uncertainty is associated with possible complications arising from PCP behavior within fish, including ionization and metabolism. These effects should be addressed with further experimentation and model refinement.

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Figure 1

Erosion & Run-off Load



Kg/day (monthly average)

Stream Flow for Heath Creek





Concentration in Stream Erosion & Run-off



Mean Concentration, mg/

CDF for Stream Concentration







Log Concentration, mg/

Chemical Concentration in Stream from Leachate Load





Trout Whole Body Concentration



Time (days)

Concentration, min 45

Trout Concentration from Leachate



Concentration, ----- 3/9

CAPPING WOOD PRESERVING SITES

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CAPPING WOOD PRESERVING SITES

INTRODUCTION

The closure of almost every contaminated site includes some type of cover system. Although sometimes referred to simply as the "site cap", the site cover is called upon to perform several functions. These may include aesthetic beautification, retention of gases or vapors from escaping out from the site, prohibition of entry of precipitation into underlying waste, provide a component of the relandscaping of an area, and others. Hydrologic isolation of underlying waste is the most common criteria applied to cap design, and the multiple components of a cover system are designed and built to support this role.

A majority of wood preserving sites lie in humid climatic regions, where reducing infiltration of rainfall is a major mechanism applied to reduce leaching and loss of contaminants to the groundwater plume.

BACKGROUND DOCUMENTS ON COVER SYSTEMS

The EPA's Office of Research and Development has provided several comprehensive documents which describe the design and construction of caps or covers for waste disposal sites. A pioneering effort first published in 1979 (USEPA, 1979) still remains a good foundation for cover design. The Agency's Office of Solid Waste has issued a guide for evaluating cover systems (USEPA, 1982). More recently, ORD has issued a technical resource document directed specifically toward covers on uncontrolled hazardous waste sites, of which wood preserving sites comprise a subset (USEPA, 1985). An in-depth presentation of factors important in design, construction, and testing of compacted soils built as a barrier to infiltration of rainfall into underlying wastes is contained in a technical resource document primarily aimed at landfill liner structures (USEPA, 1986). A Seminar series (USEPA, 1988) presented throughout the United States during 1988 compiles and summarizes much of the material presented in detail in the above references.

COVER SYSTEMS IN HUMID REGIONS

The primary intent of nearly every cover system is to keep precipitation out of the underlying waste material. Cover system designs to accomplish this goal consist of several different layers of soil and other materials, in a sort of sandwich arrangement. Figure 1 illustrates a typical series of layers designed into a current cover system for either RCRA landfills or as part of the remedy applied to old contaminated sites such as wood preserving sites. The rationale and details of each major system component are discussed in detail in the documents previously cited. Figure 2 shows a cover system developed in studies in arid regions. The cobble layer which restricts the burrowing of rodents is also likely to have an advantage in restricting moisture movement downward from overlying soil. It provides a capillary break. However this feature has not yet been studied in regions where high rainfall provides a net moisture infiltration into soil.

One aspect of these classical multi-layer designs which has received too little attention is the foundation for the cover--in most cases this is waste material deposited in a site. In the case of wood preserving sites, the foundation is likely to consist simply of chemical-contaminated native soil materials, often only little disturbed. The compacted soil barrier usually is constructed at the base of the cover system, and is the first cover system component directly overlying the waste in the landfill or the contaminated soil in a remediated site, Because of its unique function to provide as good a barrier as possible to infiltration of precipitation into underlying site material. the soil barrier must be built with a very high degree of structural integrity. This demands a sound foundation. With little experience in specifying the degree of competence required in the foundation for a compacted soil layer designed for very low permeability, we must, at present, leave this design feature to traditional structural engineering. Therefore, we must ensure that the foundation factor is adecuately presented in remedial designs for cover systems.

The topsoil layer, to support vegetation, and the compacted soil barrier layer are the parts of the cover system most often compromised in remedial designs. This is simply because they consume the most soil materials, and reductions here can easily lead to reduced overall costs.

Figure 1.



Figure 2.

1.



In the topsoil, or the total soil zone in the surface of a cover system which supports the root zone of the plants, we have a finite volume of material which is the sole support of the planted vegetation. The physical properties of this soil material need particular emphasis because the moisture holding capacity, over all seasons of the year, is critical to plant survival. Characterization of the moisture holding and release properties of the vegetated soil materials appears to be a neglected parameter in cover system design, materials selection, and construction. Vegetation established on landfill or remedial site covers needs to be considered from the aspect of plant ecology as well as immediate aesthetics. This simply means that a well manicured lawn or pasture mix of grasses is unlikely to be as successful in the long term, with low maintenance, as would be a less popular mixture such as weeds and plants found in unmaintained low fertility soils.

Specifications for materials in cover systems, such as the seeds, planting schedule and related agronomic practices need to be written in contract language. A common precedent useful to project managers unfamiliar with revegetation can be found at state highway departments. Revegetation of roadsides and highway cut and fill material would include many of the practices that need to be applied to grow plants on a soil placed as the top of a cover system. Experience also exists in regions where mined land has been regraded and plant established by contract construction firms. State Departments of Natural Resources, or Bureaus of Mines are the typical contacts for site remediation in this industry. When consulting with agencies that have related experience, academic agronomists, and mission-oriented professionals such as SCS soil surveyors or practicing soils engineers, one must continue to recognize that their expertise and orientation is likely to be much narrower than application to a waste-contaminated soil area. Therefore the remedial design reviewer must personally integrate the oriented bits of technical advice from these several related technical experiences into a plan that appears best for a particular site. The field of environmental cleanup is still young in the area of multidisciplinary technical integrators with substantial experience.

Most remedial design guidance provides idealized diagrams (Figure 3) and line drawnings of cover systems which design engineers are requested to use

Figure 3.



as the basis for cover designs on sites which are non-ideal. Few sites in the field are of uniform dimension, with no interfering natural features such as slopes, ravines, powerline right-of-ways, property boundaries, wetlands, etc. The construction blueprints we have seen leave a great deal to the imagination of the field superintendent with regard to the actual cover system material placement. A clear picture of how the various cover materials will be handled is necessary so that compromises in material and construction do not occur which compromise the intended hydrologic performance of the total cap. Included in this part of the design should be also the construction sequence. With a great deal of earth material being hauled in and moved around, there must be a preplanned clear picture of which truckload of what comes first, next, and where.

Complexities in material needs and material handling drive cover system designs to include less soil material and either amendments such as bentonite or synthetic plastic materials as the primary precipitation barriers. Each of these options generates a great deal of detailed discussion of pros and cons. Our research laboratory has investigated and published numerous reports in recent years regarding the barrier properties of a wide range of these types of materials.

Questions have arisen regarding the use of asphalt, cement, fly ash additives, and other particular materials to cap a site, either instead of, or on an area separate from that covered by a multi-layer cover system. Where a structure or parking lot or other land use requires a cap based on structural use, concrete or asphalt may be the best alternative. However we have not seen any data which show that extensive areas paved by road building practices approach the low permeability to precipitation that a well-constructed system provides. Construction practices that are classical for traffic and structural load-hearing have not been shown to provide low permeability to hydraulic flow. We are still looking for data which show that traditional measures of soil materials' engineering characteristics directly predict hydraulic containment properties. Even the measurement of hydraulic conductivity of compacted fine-grained soils has been subjected to extensive research in the laboratory and field. The results show simply that this parameter needs to be measured in each site- and material-specific case in

order to be assured that the desired low permeability can be obtained in a liner or cover structure. Concrete and asphalt laid to road building specifications are both too porous and cracked to provide a barrier to infiltration.

Questions regarding the effects of freeze/thaw on compacted soil in a cover system are just now beginning to be investigated. The preliminary studies conducted by the Corps of Engineers and DOE are not conclusive. The current best advice seems to be to insulate or cover the compacted low-permeability layer as deep as possible to be out of reach of frost. Since no definitive data yet exist on whether freezing is detrimental, placement below the "average depth of frost penetration" is the current accepted design.

The quality of the construction of RCRA waste management facilities has been studied by our Laboratory. Essential aspects of Quality Assurance/ Quality Control have not been as clearly documented for remedial design and construction activities, but we believe them to be at least as important and significant to a successful remedy as we find in RCRA facilities. We have published a document (USEPA, 1986a), which emphasizes RCRA facilities, but would be a good guide to operations under SARA which should be examined with respect to construction quality.

CONCLUSION

The references cited earlier provide a great deal of details on cover system design. The reader must be alert to areas in these writings where the civil engineering has not yet made the transition from load-bearing structures to low-leakage containment structures. Agency staff responsible for design of remedial activities applied to wood preserving sites are burdened with being the integrator of knowledge and technical information from a variety of technical disciplines and sources. This paper is intended to provide direction toward the various resources available to ease these tasks.

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STABILIZATION/SOLIDIFICATION OF METALS IN SOILS AND SLUDGES Edwin F. Barth, EPA-RREL, Cincinnati, Ohio
THE USE OF SOLIDIFICATION/STABILIZATION FOR WOOD TREATING SITES

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Edwin F. Barth, P.E. Risk Reduction Engineering Laboratory Cincinnati, Ohio 45268 Solidification/stabilization technology may be a viable alternative for many corrective actions at uncontrolled hazardous waste sites. Solidification implies the hardening of a waste matrix, which may also decrease contaminant leaching while stabilization implies a chemical reaction to decrease chemical leaching.

Solidification/stabilization using pozzolanic material is generally considered applicable for soils contaminated with heavy metals. However, the physical and chemical characteristics of each soil matrix makes upfront treatment predictions difficult. A solidification/stabilization study for the Office of Solid Waste's BDAT Program (see Table 1) was effective for reducing TCLP leachates for As, Pb, Cu, Cd and Zn^1 in the BDAT contaminated soil matrix. However, CCA contaminated soils contain two metals that are thought to be difficult to stabilize arsenic and chromium as Cr^{+6} .

There are many unknowns when considering solidification/stabilization for organic wood treating waste. High concentrations of oil and grease can impede the setting of a curing sample². In general, pozzolanic material may only solidify, but not stabilize an organic waste. Pozzolanic material was not successful in decreasing TCLP leachate concentrations of semivolatile compounds¹ in the BDAT study.

The state-of-the-art of solidification/stabilization for organic waste is the use of alternative binding agents such as surfactants, polymers, or modified clays (organophilic clays). Recent studies have shown promise for modified clays^{3,4}. Table 2 shows that the TCLP leachate of some organic compounds may be substantially reduced after stabilization with a modified clay. Asphaltic material has been evaluated for stabilizing dioxin contaminated soil⁵, which could be present on a creosote site.

The major issues involving the stabilization of hazardous waste is the permanence or long term stability of the treated waste. This depends on many factors, such as the binder used, potential redox reactions, waste setting and management controls. As yet, no leachate test or set of tests have been agreed to mimic long term disposal conditions.

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Sample Binder		;	Arsenic Cad			mium		Chromium		Copper		Lead			Nickel		Zinc			
No.	(Day)	:	a	Ь	8	b		a	Ь		a	Ь		8	Ь		8	Ь	a	Ь
I	RAW	;	ND	و میند درو بای سو دی	; 0.53	ین بین مرد مرد مرد ا	;	ND		;	0.61		;	0.49		:	0.27		9.2	
1	PC(14)	:	ND	-	I ND	100	;	0.06	+	;	0.07	81	:	0.15	75	: (0.04	70 :	0.23	96
14	KD(14)	;	ND	-	I ND	100	:	0.06	+	;	0.04	81	:	ND	100	:	ND	100 :	0.27	9
27	LF(14)	1	ND		: ND	100	:	0.02	+	:	0.03	98	t	ND	100	;	ND	100 :	0.14	94
1	PC(28)	;	ND	-	: ND	100	;	0.06	+	:	0.06	83	ŀ	0.15	75	:	0.04	70 :	0.49	9
15	KD(28)	;	ND	-	: ND	100	;	0.09	+	:	0.03	80	;	ND	100	1	ND	100 :	0.62	7
27	LF(28)	;	ND	-	: ND	100	;	0.02	+	:	0.03	98	:	ND	100	:	ND	100 :	ND	10
II	RAW	:	ND		0.73		;	ND		:	0.89		;	0.7		; (0.4	;	14.6	
4	PC(14)	;	ND	-	: ND	100	:	0.03	+	;	0.04	92	1	0.15	82	:	0.04	83 ;	0.09	9
16	KD(14)	:	ND	-	: ND	100	1	0.08	+	:	0.07	79	:	0.44	+	:	ND	100 ;	0.25	9
30	LF(14)	:	ND	-	: ND	100	;	ND	~	:	ND	100	:	ND	100	:	ND	100 :	0.22	9
4	PC(28)	:	ND	-	: ND	100	ł	0.03	+	t	0.06	89	1	0.15	83	: 1	0.04	83 :	0.54	9
16	KD(28)	;	ND	-	I ND	100	1	0.05	+	1	0.09	89	:	0.37	+	;	ND	100 :	0.78	8
29	LF(28)	:	ND	-	: ND	100	;	ND	-	;	0.03	90	;	ND	100	:	ND	100	0.02	10
III	RAW	;	6.39		: 33.1		;	ND		;	80.7		1	19.9		: 1	7.5	:	359	
7	PC(14)	:	ND	100	: ND		;	0.07	+	ł	0.15	100	:	0.63	95	:	ND	100 :	0.58	10
21	KD(14)	:	ND	100	: ND	100	:	0.22	+	;	1.02	96	f	13.3	+	1	ND	100 :	4.38	9
33	LF(14)	;	0.81	52	0.02	100	;	0.03	+	;	2,96	87	;	51	+	:	ND	100 :	3.81	9
7	PC(28)	1	ND	100	I ND	100	:	0.07	+	:	0.09	100	;	ND	100	;	ND	100 :	0.69	10
21	KD(28)	:	0.21	98	: ND	100	;	0.12	+	:	0.85	96	;	18.3	+	;	ND	100 :	4.07	9
33	LF(28)	:	0.79	51	: 0.02	100	:	0.07	+	ł	2.59	87	;	51	+	:	0.03	99 :	3.97	9
IV	RAW	;	9.58		35.3		;	0.06		;	10		1	70.4		: 2	6.8		396	
10	PC(14)	:	ND	100	: ND	100	1.	0.06	+	:	0.14	100	:	0.39	9 9	:	ND	100 ;	0.39	10
23	KD(14)	;	0.16	95	I ND	100	;	0.11	+	:	1.88	97	!	12.4	43	:	ND	100 ;	4.57	9
	LF(14)	:	1.61	50	: ND	100	:	0.07	+	:	1.92	96	;	91.8	+	:	ND	100 ;	3.22	9
10	PC(28)	ł	ND	100	: ND	100	;	0.06	+	:	0.17	100	:	0.37	9 9	:	ND	100 :	0.74	10
23	KD(28)	;	0.27	92	: ND	100	;	0.12	+	;	1.67	97	;	21.4	9	1	ND	100 :	3.72	9
	LF(28)	;	0.98	59	0.02	100		0.07	+	1	2.18	95	;	65	+	:	ND	100 :	3.64	9
Detect	ion Limi	it	0.15		: 0.01		1	0.01		Ì	0.02		:	0.15		;	0.04		0.01	

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TABLE 1. SUMMARY OF TCLP RESULTS FOR METALS

TABLE 2.

S/S DATA - WHITEHOUSE, FLORIDA

	RAW (ppb)	TWA (ppb)	TCLP (ppb)
Bis-ether	8,528	ND	ND
Naphthalene	18,060	1,445	ND
Phenanthrene	20,184	ND	ND
Benzo-anthracene	30,460	ND	ND
Source: reference 4			



STABILIZATION/SOLIDIFICATION OF METALS IN SOILS AND SLUDGES

by

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S/S PURPOSE

TO DECREASE LEACHING:

SOLIDIFICATION (NONSOLID → SOLID)

VS.

STABILIZATION (CHEMICAL REACTION)

S/S APPLICABILITY

- Lead (Pb)
- Nickel (Ni)
- Zinc (Zn)
- Copper (Cu)
- Cadmium (Cd)
- Chromium(III) (Cr⁺³)
- Low-level organics

- Chromium(VI) (Cr⁺⁶)
- Arsenic(III) (As+3)
- Arsenic(V) (As⁺⁵)
- Mercury (Hg)
- High-level organics

CHEMICAL REACTION MECHANISMS

• PRECIPITATION AS:

HYDROXIDES (OH) SILICATES (Si) SULFIDES (S)

- COMPLEXATION
- ORGANIC BINDING

S/S OF ORGANIC MATERIAL

IN GENERAL, POZZOLANIC MATERIAL WILL NOT BIND ORGANICS; AN ORGANOPHILIC BINDER MUST BE USED FOR STABILIZATION.

NOTE: PCB DECHLORINATION?

S/S INTERFERING COMPOUNDS

- SULFATES (SO₄)
- NITRATES (NO₃)
- PHENOLS
- OIL & GREASE

SOIL VARIABLES IMPACTING S/S

- GRAIN SIZE DISTRIBUTION
- COHESIVENESS
- CATION EXCHANGE CAPACITY (CEC)
- "ACID" CONTENT (HUMIC, FULVIC)
- PARTITIONING (TOTAL ORGANIC CARBON)

S/S OF CREOSOTE WASTE

- Cu
- $Cr^{+6} \rightarrow Cr^{+3}$
- As + complex
- PCP (oily)

S/S LEACHING/EXTRACTION VARIABLES

- MONOLITHIC VS. GRINDING
- DYNAMIC VS. STATIC
- TYPE AND PREPARATION OF EXTRACT

S/S LEACHING/EXTRACTION TESTS

- EXTRACTION PROCEDURE (EP) TOXICITY
- TOXICITY CHARACTERISTIC LEACHING PROCEDURE (TCLP)
- MONOFILLED WASTE EXTRACTION PROCEDURE (MWEP)
- TOTAL EXTRACTION
- ANSI 16.1
- MCC-1P
- EQUILIBRIUM LEACH TEST
- SEQUENTIAL CHEMICAL EXTRACTION

S/S PHYSICAL TESTS

- UNCONFINED COMPRESSIVE STRENGTH (UCS)
- PERMEABILITY
- WET/DRY
- FREEZE/THAW
- COMPACTION
- DENSITY

TCLP LEACHING PROCEDURE



PHASE I BDAT CHEMICALS

METALS PbSO₄ ZnO CdSO₄ As₂O₃ CuSO₄ Cr₂O₃ Ni (NO₃)₂

VOLATILES

ACETONE CHLOROBENZENE 1,2-DICHLOROETHANE ETHYLBENZENE STYRENE TETRACHLOROETHYLENE XYLENE

SEMIVOLATILES

ANTHRACENE BIS-PHTHALATE PENTACHLOROPHENOL (PCP)

S/S DATA - WHITEHOUSE, FLORIDA

	RAW (ppb)	TWA (ppb)	TCLP (pph)
Bis-ether	8,528	ND	ND
Naphthalene	18,060	1,445	ND
Phenanthrene	20,184	ND	ND
Benzo-anthracene	30,460	ND	ND

ORGANOPHILIC CLAY



SUPERFUND CREOSOTE SITES EVALUATING S/S

- SHERIDEN DISPOSAL
- AMERICAN CREOSOTE
- J. H. BAXTER
- PALMETTO WOODS

CONTRACT SPECIFICATIONS

PERFORMANCE SPECS

VS.

TIGHTLY WRITTEN SPECS

BUYER BEWARE

- RELEASE OF VOLATILES
- DILUTION
- PCB ANALYTICAL TECHNIQUES
- PROPRIETARY AGENTS
- COST

SLURRY WALLS, RECOVERY WALLS, INTERCEPTOR TRENCHES,

AND GROUT CURTAINS

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SLURRY WALLS FOR GROUNDWATER ISOLATION AT WOOD-PRESERVING SITES

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INTRODUCTION

Vertical barriers to groundwater and pollutant migration have become common structures for isolation of groundwater contaminants. Within EPA's Superfund program, containment of liquids within a site has been accepted as a practical means to meet two goals: 1) to reduce the migration of groundwater pollutants from a site during the time that a treatment, destruction, or removal technology is being applied; and 2) to reduce the volume of groundwater coming into and through a site, so that less total volume needs to be treated for pollutant destruction or removal.

The "slurry trench cut-off wall" has been adopted from the standard civil engineering practice as the most common groundwater barrier. This structure consists of a trench maintained open by addition of a clay slurry during excavation; after reaching the desired depth and linear extent, the trench is backfilled with a material of lower groundwater permeability than the original soil or geologic formation that was excavated. The use of suspended clay slurries to maintain open excavation in coarse-grained and saturated soils has been extensively discussed in construction engineering literature (Gill, 1978; Millet et al., 1981; Ryan, 1976). The trench backfill commonly consists of a mixture of soil excavated from the trench with bentonite clay and other fine-grained materials designed to provide a relatively even distribution of many different soil particles in the final backfill mix. In specific circumstances, Portland cement has been a major backfill component where structural rigidity was required of the trench area. Other vertical barrier excavation or construction techniques and barrier material formulation have

been applied by various commercial companies and for particular site conditions (Case International, 1982).

A substantial mobilization of construction equipment is needed to install a slurry trench cut-off wall. The corporate brochure of International Technology (IT) Corporation contains a color photograph which shows the entire installation construction activity at a site where they installed 1600 lineal feet of barrier (International Technology Corporation, 1986). Figure 1 depicts the various activities at this site where 3.6 acres was encircled to a depth of 100 ft.

Slurry Trench

This method of excavation has been used by civil engineers for many decades. It is economical where the soil material is so friable that the walls of an open trench will collapse during excavation unless they are shored up by some means. Sheets of plywood or steel panels are very expensive, and can be dispensed with where the excavation is a narrow trench that can be filled with a suspended clay during excavation. Common trench excavators can continue to dig through a water-filled trench. Traditionally, bentonite clay has been the routine material added to the trench to maintain it open until a backfill material has been placed. Numerous reports of experience with this material have been published (D'Appolonia, 1980). Recently, other materials such as attapulgite clay plus surfactants, and protein-rich gum material from organic and biochemistry processes have been tested or used at particular slurry trench projects.

Cut-Off Wall

The backfill or other material placed within a trench excavated in a water slurry creates the groundwater barrier desired at a site under remedial action. The most common trench backfills consist of a mixture of soil and bentonite clay (SB) or portland cement, bentonite clay, and soil material (CB). Soil/bentonite backfill normally consists of the soil material obtained during trench excavation along with commercially obtained bentonite clay added to increase the content of fine-grained particles. Locally obtained clay from a borrow pit is also often added to increase the fines content of the backfill. Ideal SB backfills should contain an assortment of



Figure 1. Equipment and activities at the site of construction of a slurry trench cut-off wall.

soil materials that includes an even distribution of the range of soil particle sizes. This assortment has the greatest potential for all pore space in the backfill to be occupied by solids, thus reducing permeability to the groundwater. Backfill containing sufficient cement or other pozzolan to harden in place is often used either where structural strength is desired in the completed barrier, or there may be inadequate amounts of soil materials available at economic rates. Recent engineering designs have included interlocked sheets of synthetic flexible membrane liner materials (FML) inserted into the slurry trench to provide a water migration barrier of lower permeability than obtainable with soil or cement mixtures. Use of such synthetic barriers in slurry trenches is very young and only one or two examples have so far been reported in technical journals.

The utility of bentonite clay in slurry trench construction must be mentioned because of the great commercial market for this commodity. The physical and chemical properties of bentonite were characterized by geologists and clay mineralogists many decades ago. Their data were immediately applied by engineers, primarily oil well drillers, where "drilling mud" was enriched with bentonite because of its capability to both lubricate the drill stems and carry suspended drill cuttings out of deep wells to the surface. This use remains a very large market. Bentonite clay is the commercial or colloquial name for naturally-occurring clay deposits which contain the clay-sized mineral montmorillonite as the dominant constituent. Volumes of technical literature exist which present almost any aspect of bentonite clay and montmorillonite mineralogy (e.g., Jepson, 1984). The action of bentonite clay in a slurry trench to maintain the trench open during excavation has been discussed in detail in engineering publications (Millet et al, 1981). In recent years, other materials have been suggested and tried for use as a slurry trench water suspension agent. Bentonite remains favored by many designers because when some of the trench slurry is used in mixing the backfill. some amount of bentonite is included, which adds to the fines content of the backfill, providing a lower permeability of the final backfill mixture.

SLURRRY TRENCH CUT-OFF WALLS FOR POLLUTION MIGRATION CONTROL

Early in the consideration of engineering technologies and structures that could be applied to clean up uncontrolled hazardous waste sites, the

"slurry trench cut-off wall" was included in remedial designs (U.S. EPA, 1984). This structure was included for one or both of two groundwater control reasons: 1) to restrain contaminated groundwater from leaving a site so that the groundwater cleanup technologies could be activated, and 2) to reduce the quantities of offsite groundwater entering the site, thus reducing the dilution of contaminants and the total amount of contaminated groundwater that would need to be treated to remove pollutants.

Slurry walls as barriers early resulted in studies of the degree to which groundwater flow was reduced, which lead to laboratory measurement of the permeability of backfill materials. Traditional methods of study of soil permeability were applied, and many data were published, with some studies continuing today. Laboratory permeability testing is a routine operation in characterizing a proposed backfill mixture. A major consideration is whether the site groundwater contaminants are chemically aggressive and will react with backfill components (reaction with bentonite clay is a major concern), leading to reduced permeability after backfill installation. Several published reports present the current state-of-the-art in laboratory permeability testing (Carpenter, 1986; Daniel, 1984; Evans, 1986).

The actual hydraulic attenuation performance of an installed cut-off wall has been documented in very few cases.

Compatibility Testing

The laboratory permeability test of cut-off wall backfill materials has become the primary measure of compatibility of the barrier with the groundwater in which it will be in contact. Although several studies have reported the influence of permeant liquid composition on the hydraulic conductivity of cut-off wall backfill mixtures, a great deal of the concern for the potential for adverse chemical interactions derives from studies of solvent effects on compacted clay soil landfill liners. Grube, 1987, summarized these numerous studies. If the groundwater contains solutes that will degrade the barrier, this factor should be determined early in the design stage of the cut-off wall. Acceptance of a cut-off wall within remedial designs usually requires submission of data showing that the selected backfill does not change permeability after the permeant fluid has been passed through. The permeant liquid is usually chosen to be either actual contaminated groundwater from a site or a synthetic mixture created to simulate chemically aggressive groundwater. There does not appear to be a well-recognized universal formula for mixing laboratory reagents to simulate an aggressive groundwater; each formulation is generally site-specific. Evans and Fan, 1986, present a description of the laboratory method that is widely applied to determine groundwater/barrier compatibility.

A particular situation in which compatibility testing of both trench slurry and backfill is essential lies in regions where the marine environment is a strong influence on groundwater composition. Since sodium-bentonite will lose this cation and corresponding swelling capacity in the presence of cations such as calcium and magnesium from sea water, the extent of this exchange must be determined early in the design of a cut-off wall in this environment. Commercial bentonite clay suppliers claim they both have bentonite clay formulations which resist ion exchange in marine environments and also provide laboratory testing services to demonstrate the performance of their products. The cut-off wall designer should be sure that compatibility tests are conducted in an unbiased manner and that procedures well recognized for relevance are used.

A special area requiring attention in the case of wood-preserving sites is the potential presence of immiscible liquids sunken or floating in the site groundwater. These liquid pollutants can be either penta- or other chlorophenols, probably with diesel fuel floating on the phreatic surface or creosote-based residues pooled on the surface of a less-pervious geologic strata at some depth in the site's groundwater. It is clear that where a cut-off wall intersects such immiscible pools of contaminants, the potential for chemical degradation of the barrier is high, and will not be reflected by tests of trench slurry or backfill mixtures where normal groundwater from the site has been used. In sites where there is a possibility of the presence of immiscible pools, there must be sufficient credible data from groundwater regime characterization to identify them. In the past, there has not appeared to have been much concern for determining localized contaminant regions during site characterization, but this must be considered in barrier design.

In-Situ Performance Monitoring

Data which show the degree to which an installed groundwater cut-off barrier has been effective are sparse in open published technical journals. Barrier effectiveness has been evaluated in terms of how much lower the concentration of certain solutes is in monitoring wells outside the cut-off wall versus inside the structure. Another measure has been the decrease in groundwater elevation inside the structure relative to the ambient outside.

Probably the most well-documented study of the hydrologic effect of cut-off wall installation at a Superfund site is that which the EPA's Office of Research and Development conducted at the Sylvester Site in Nashua, New Hampshire (U.S. EPA, 1987).

Both the U.S. Army Corps of Engineers in individual districts, and private corporations who plan installation of groundwater containment or isolation barriers have required pilot-scale construction of barriers in order to qualify construction contractors. These pilots consist of an area, perhaps 50 feet square, surrounded by a cut-off wall built by a contractor in a manner similar or equal to what we would build if granted a contract for several thousand lineal feet of barrier. The "test box" has monitoring wells installed both inside and outside, and pump-down tests are conducted on well(s) inside the "test box". Data obtained from well water levels are used to calculate the permeability of the barrier system, and results are compared with design expectations or regulatory requirements. Data from Corps of Engineers projects repose in the individual district and site files, and data from private corporations are largely unavailable except perhaps in local or state permitting agency files.

It is known that data have been collected at full-scale groundwater cut-off wall installations, which would document the barrier's hydrologic performance. Sites such as Rocky Mountain Arsenal, Lipari Landfill Superfund Site, and several installations by private corporations to meet individual states' remedial requirements have generated data which have not been fully reported in open technical journals. The extent to which particular regional or state regulatory agencies have compiled or summarized these data is unknown.

CONCLUSIONS

Groundwater barriers constructed using slurry trench techniques have been routinely constructed by civil engineers for many years. Since the late 1970's, an undocumented number (perhaps in the range of 20 to 30) have been installed specifically to control the migration of groundwater contaminated with hazardous waste solutes.

Testing the barrier filling mixture to verify that it will not significantly change permeability in the presence of the site contaminated groundwater relies primarily on laboratory permeability test procedures. Methods for these procedures have not been formally standardized. Reports of studies in geotechnical journals form the basis for conducting compatibility tests.

Data which illustrate the effectiveness of a cut-off wall after installation are largely unsummarized and repose within individual site files of cognizant regulatory offices. Methods to reliably measure and document the in situ hydrologic performance of groundwater barriers have not been clearly developed and published.

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APPENDIX A

SUPPLEMENTARY MATERIAL FOR OVERVIEW OF THE WOOD PRESERVING INDUSTRY Dr. Gary D. McGinnis, Mississippi State University

2389-109920

EPA/600/2-88/055 September 1988

CHARACTERIZATION AND LABORATORY SOIL TREATABILITY STUDIES FOR CREOSOTE AND PENTACHLOROPHENOL SLUDGES AND CONTAMINATED SOIL

by

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WOOD PRESERVING INDUSTRY

Introduction (Burdell, 1984)

Wood preserving in the United States is a hundred-year-old industry. Wood is treated under pressure in cylinders with one of four types of preservatives: 1) creosote, 2) pentachlorophenol in petroleum, 3) water solutions of copper, chromium, and arsenic (CCA), and 4) fire retardants.

The 1978 volume of wood commodities treated is shown in Table 1 (USDA, 1980).

Product	Volume treated with Creosote solutions Penta Inorganic salts ^a 1,000 cu. ft					
Crossties, switch ties, and land- scape ties	103,138	449	2,498			
Poles Crossarms Piling	18,237 41 9,993	41,905 1,615 1,154	4,038 29 943			
timbers Fence posts Other products	10,780 4,584 <u>7,815</u>	21,209 10,983 2,681	73,317 4,461 7,616			
Total (1980)	154,587	79,996	92,903			

Table 1. Volume of wood commodities treated in 1978.

^aThe main inorganic salts are copper, chromium, and arsenic.

About 99% of the creosote solutions, 90% of the penta, and all of the arsenical salts in the preceding tabulation are applied by pressure methods in closed systems. A small amount of creosote and about 3.8
million pounds of penta are applied by commercial thermal and dip treatment methods in open tanks.

Basic Wood-Treating Process

The basic oil-preservative wood-treating cycle begins by placing either seasoned or green wood into a pressure cylinder. If green materials are used, they can be artificially seasoned in the cylinder with steam and either oil preservative or hydrocarbon vapor. Then an initial air pressure (vacuum or positive pressure) is introduced into the system. Next the preservative is pumped into the cylinder and the pressure increased until a predetermined liquid volume is absorbed into the wood. The pressure is released and the preservative is pumped back into the tanks. A final vacuum is applied to remove most of the free liquid on the surface.

The organic preservative most used is coal tar creosote, a byproduct from the production of coke from coal. When coal tar is distilled, the 200° to 400° C fractions are creosote. Creosote is mostly aromatic single to multiple ring compounds. Over 200 different components have been identified in creosote.

Pentachlorophenol dissolved in No. 2 fuel oil carrier is the second most common organic wood preservative. Technical grade PCP is about 85 to 90% pure PCP plus various levels of other chlorinated phenolic compounds.

CHARACTERISTICS OF THE ORGANIC WOOD PRESERVATIVES

The two major organic wood preservatives used in the United States are pentachlorophenol (PCP) and creosote.

Technical-grade PCP used for treating wood contains 85 to 90% PCP. The remaining materials in technical grade PCP are 2,3,4,6tetrachlorophenol (4 to 8%), "higher chlorophenols" (2 to 6%), and dioxins and furans(0.1%). The tetrachlorophenol is added to PCP to increase the rate of solubilization.

The other contaminants found in technical-grade PCP are formed during manufacture. In the United States PCP is manufactured from phenol by a catalytic chlorination process. During chlorination, the temperature must be maintained above the melting point of the products formed: this, it is felt, contributes to the side reaction that gives rise to contaminants, including traces of trichlorophenol, chlorinated dibenzo-p-dioxins, chlorinated dibenzofurans, chlorophenoxy phenols, chlorodiphenyl ethers, chlorohydroxydiphenyl ethers, and traces of even more complex reaction products of phenol. Chlorodibenzodioxins and furans are the by-products about which there are the greatest concerns. Analyses of PCP have revealed that the principal chlorodibenzodioxin and chlorodibenzofuran contaminants are those containing six to eight chlorines. The highly toxic 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) has not been identified in any sample of PCP produced in the United States that has been analyzed (USDA 1980). The composition of a sample of commercial PCP and of a sample of purified PCP is given in Table 2. A representative distribution of isomers is given in Table 3 (U.S. EPA 1978).

The physical properties of a compound play an important role in how the compound behaves under different conditions. These properties influence the mobility of a compound in air or water, its ability to adsorb to surfaces, and its susceptibility to degradation. These

Component	Analytical results				
	Commercial ^a (Dowicide 7)	Purified ^b (Dowicide EC-7)			
Pentachlorophenol	88.4%	89.8%			
Tetrachlorophenol	4.4%	10.1%			
Trichlorophenol	0.1%	0.1%			
Chlorinated phenoxyphenols	6.2%				
Octachlorodioxin	2500 ppm	15.0 ppm			
Heptachlorodioxins	125 DDM	6.5 ppm			
Hexachlorodioxins	4 pom	1.0 mm			
Octachlorodibenzofuran	80 ppm	1.0 ppm			
Heptachlorodibenzofurans	80 ppm	1.8 ppm			
Hexachlorodibenzofurans	30 ppm	1.0 ppm			

Table 2. Comparison of composition of commercial grade and purified grade pentachlorophenol (U.S. EPA 1978).

^aSample 9522A. ^bTechnical grade PCP purified by distillation.

Table 3.	Chlorodioxin isomer distributions	in
	commercial grade PCP (Dowicide 7)	
	and rurana samples (buser	
	1975, 1976).	

Chlorodioxin	PCP ^a (ppm)	PCP-Na ^b (ppm)
1,2,3,6,7,9-C1 ₆ D	1	0.5
1,2,3,6,8,9-C1 ₆ D	3	1.6
1,2,3,6,7,8-C1 ₆ D	5	1.2
1,2,3,7,8,9-C1 ₆ D	0	0.1
1,2,3,4,6,7,9-C17D	63	16.0
1,2,3,4,6,7,8-C17D	171	22.0
1,2,3,4,6,7,8,9-C1 ₈ D	250	110.0

^aDowicide 7 (commercial PCP).

^bSodium salt of PCP.

factors are important because they relate to the route and rate of exposure by which a compound might be received by man or other organisms. Some of the selected physical properties of pentachlorophenol are given in Table 4.

Pentachlorophenol is quite stable. It does not decompose when heated at temperatures up to its boiling point for extended periods of time. Pure PCP is considered to be rather inert chemically (Bevenue and Beckman, 1967). The chlorinated ring structure tends to increase stability, but the polar hydroxyl group tends to facilitate biological degradation (Renberg, 1974). It is not subject to the easy oxidative coupling or electrophilic substitution reactions common to most phenols. All monovalent alkali metal salts of PCP are very soluble in water, but the protonated (phenolic) form is virtually insoluble. Hence, transport of PCP in water is related to the pH of the environment.

Pentachlorophenol is moderately volatile and a closed system should be used when heating environmental samples or recoveries will be poor (Bevenue and Beckman, 1967). By contrast to other chlorinated organic compounds of low vapor pressure, PCP can be lost from soils by volatilization (Briggs, 1975).

Creosote

The other major organic wood preservative used in the United States is creosote. Creosote, in contrast to PCP, is a very complex mixture of organic compounds produced from coal.

At least 200 chemical compounds have been identified in creosote. Although the chemical composition of this material varies for reasons discussed above, it is generally agreed that creosote contains several

Property	Value
Empirical formula	с6сі5он
Molecular weight Melting point Boiling point Density pK _A (25 ⁰)	255.36 190 ⁰ C 293 ⁰ C 1.85 g/cc 4.70-4.80
Partition coefficient (Kp), 25 ⁰ Octanol-water Hexane-water	1760 1.03 × 10 ⁵
Vapor pressure, Torr (mm hg) 0°C 20°C 50°C 100°C 200°C 300°C	1.7×10^{-5} 1.7×10^{-4} 3.1×10^{-3} 0.14 25.6 758.4
Solubility in water (g/L) 0°C 20°C 30°C 50°C 70°C	0.005 0.014 0.020 0.035 0.085
Solubility in organic solvents (g/100g solvent) in methanol 20°C in methanol 30°C in diethylether 20°C in diethylether 30°C in ethanol 20°C in ethanol 30°C in acetone 20°C in acetone 30°C in xylene 20°C in xylene 30°C in benzene 20°C in benzene 30°C in benzene 30°C in carbon tetrachloride 20°C in carbon tetrachloride 30°C	57 65 53 60 47 52 21 33 14 17 11 14 17 11 14 2 3

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Table 4. Physical properties of PCP (Crosby 1981; Bevenue et al. 1967).

thousand different compounds which could be identified with GC/MS. Most of these are present in very small amounts. The major components of a typical creosote of U.S. origin and one of German origin are shown in Table 5. There are some rather striking differences between the two types of creosote in the levels of particular polycylic aromatic hydrocarbons and in the overall levels of total PAH's.

The greater part of the composition of creosote consists of neutral fractions. Tar acids, such as phenol and the cresols, as well as such tar bases as pyridenes, quinolines, and acridines, constitute a rather small percentage of the total weight of creosote.

A schematic of the distillation processes is presented in Figure 1. Creosote is a blend of the various distillates designed to impart specific physical characteristics that meet standards of the American Wood-Preservers' Association (AWPA).

Compared to the starting material, the yield of fractions that are blended to make creosote ranges from 25 to 40%, depending upon the point at which distillation is terminated. Both the yield and the chemical and physical properties of the various fractions are influenced by the characteristics of the coal from which the tar originates, the type of equipment used in the distillation process, and the particular process used.

There were 64 producers of coal tar in the United States in 1972 and 24 tar distillation plants producing creosote (U.S. EPA, 1975). Because their chemical composition and properties are not uniform, creosote and blends of creosote and coal-tar are normally described in terms of their physical properties. American Wood-Preservers' Association specifications for creosote for various uses are given in

Compound or component	U.S. creosote ^a	of total German creosote ^b
Naphthalene	3.0	7.3
Methyl naphthalene	2.1	4.2
Diphenyl dimethylnaphthalene	••	3.2
Bipheny]	0.8	
Acenaphthene	9.0	4.1
Dimethylnaphthalene	2.0	-
Diphenyloxide	**	3.4
Dibenzofuran	5.0	-
Fluorene-related compounds	10.0	9.6
Methyl fluorenes	3.0	
Phenanthrene	21.0	12.6
Anthracene	2.0	
Carbazole	2.0	
Methylphenanthrene	3.0	5.4
Methyl anthracenes	4.0	
Fluoranthene	10.0	6.8
Pyrene	8.5	5.0
Benzofluorene	2.0	4.6
Chrysene	3.0	2.8
Total	90.4	69.0

Table 5. Chemical composition of a United States and a German creosote.

^aLorenz and Gjovik, 1972. ^bBecker, 1977.





Table 6. Similar standards have been promulgated by the American Society for Testing and Materials (ASTM) and the General Services Administration (GSA). The principal differences among creosotes for the three uses shown are in specific gravity and the fraction of the oil distilled within various temperature ranges.

A comparison of physical properties of creosote and creosote/coal tar mixtures as shown in Table 7 indicates much higher distillation residue for coal tar. A list of the properties of some of the 16 priority pollutant PAH compounds found in creosote is given in Table 8 (Sims et al., 1987).

Another group of compounds which have been identified in creosote and which are related to the PAH's are the azaarenes which make up approximately 0.13% of creosote (Adams et al., 1984). These compounds are polycyclic hydrocarbons containing nitrogen (e.g., quinoline and acridine).

CHARACTERISTICS OF WOOD-PRESERVING WASTES

There are several sources of contamination at wood-treating sites. During the treatment cycle, waste water with traces of preservative in water is produced from several sources, from the live steaming of the wood, from vapor drying or oil seasoning, from vacuum condensate, from steam and oil leaks around the system, from cleanup, and from contaminated rain water. Treatment of this plant water produces sludges that are classified by EPA as KOO1, Hazardous Waste.

Prior to the environmental rules on wastewater discharge, the treating plant wastewater effluent generally went directly to surface drainage or a stream. A large number of the plants had sumps or ponds

	American Wood-Preservers' Association Standards					lards
	P1-	65 ^a	P7-	72 ^b	P13	-65 [°]
Water % volume	<	1.5	<	1.0	<	1.5
Xylene, insoluble, % by wt.	< (0.5	<	0.5	<	0.5
Specific gravity 38/15.5°C						
Whole creosote	> 1	.050	> 1	.060	> 1	.080
Fraction 235-315°C	> 1	.027			> 1	.030
Fraction 315-355°C	> 1	.095			> 1	.105
Residue above 355°C					> 1	.160
Distillation, % by wt.	Min.	Max.	Min.	Max.	Min.	Max.
Up to 210°C		2.0		1.0		2.0
235°C	~ -	12.0		10.0	~ ~	12.0
270°C	20.0	40.0			20.0	40.0
315°C	45.0	65.0			45.0	65.0
355°C	65.0	82.0	65.0		65.0	75.0

Table 6. Physical properties of creosote and its fractions. (USDA 1980)

^a For land and fresh water use.

^b For brush or spray application.

^C For marine (coastal water) use.

			Grade			
		Α	8	С	D	
Composition					*	
Creosote	100%	<80	<70	<60	> 50	
Coal tar	~-				***	
Water (% by volume)		>3.0	>3.0	>3.0	>3.0	
Xylene, insol. (% by weight)		>2.0	>3.0	>3.5	>4.0	
Coke residue (% by weight)	0.99	>5.0	>7.0	>9.0	>11.0	
Specific gravity 38/15.5 ⁰ C						
Whole oil	1.102	1.06-1.11	1.07-1.12	1.08-1.13	1.09-1.14	
235-315 ⁰ C	1.054	1.025	1.025	1.025	1.025	
315-355 ⁰ C	1.133	1.085	1.085	1.085	1.085	
Residue					~-	
Distillation						
To 210 ⁰ C	1.87	5	5	5	5	
To 235 ⁰ C	6.89	25	25	25	25	
To 270 ⁰ C	19.39			** =		
To 315 ⁰ C	49.8	36	34	32	30	
To 355 ⁰ C	72.58	60	56	52	48	
Residue	26.67					

Table 7. American Wood-Preservers' Association specifications for creosote-coal tar solutions.^a

^aLoren and Gjovik, 1972.

		Molecular Weight	Aqueous Solubility mg/l	Helting Point OC	Boiling Point [*] ^O C	Vapor pressure @ 20°C torr	Log K _{OW} *	Length of Molecule A ⁰	K _{oc}
1. <u>Two Rings</u> Naphthalene		128	31,700	80	218	4.92x10 ⁻²	3.37	8.0	1,300*
2. <u>Three Rings</u> Acenaphthylene		152	3,470	92	265 2	2.9x10-2	4.07		
Acenaphthene	R	154	3,930	96	279	2.0x10 ⁻²	4.33		
Fluorene		166	1,980	116	293	1.3x10-2	4.18		
Anthracene		178	73	216	340	1.96x10 ⁻⁴	4.45	10.5	2,600 ⁺
Phenanthrene		178	1,290	101	340	6.80x10 ⁻⁴	4.46	9.5	23,000+

Table 8. Properties of 16 priority pollutant PAH compounds. (Sims 1987).

	Holecular Weight	Aqueous Solubility* mg/l	Nelting Point OC	Bailing Point [*] ^O C	Vapor pressure @ 20°C torr	Log K _{ow} *	Length of Molecule A ⁰	K _{oc}
3. <u>Four Rings</u> Fluoranthene	202	260	111	6	5.0x10-6	5.33	9.4	
Pyrene	202	135	149	360 6	5.85x10 ⁻⁷	5.32	9.5	62,700 [#] 84,000*
Benz(a)anthracene	228	14	158	400 5	.0x10 ⁻⁹	5.61	11.8	
Chrysene	228	2	255	6	. 3x10-7	5.61	11.8	
4. <u>Five Rings</u> Benzo(b)fluoranthene	252	1.2	167	5	. 0x10 ⁻⁷	6.57		
Benzo(k)fluoranthene	252	0.55	217	480 5	.0x10 ⁻⁷	6.84		

Table 8. (continued)

Table 8. (continued)

		Molecular Weight	Aqueous Solubility* mg/l	Melting Point [®] ^{OC}	Boiling Point" °C	Vapor pressure @ 20 ⁰ C torr	Log K _{OW} *	Length of Molecule A ^O	K _{oc}
Benzo(a)pyrene		252	3.8	179	496	5.0x10-7	6.04		4,510,651
Oibenz(a,h)anthracene	9m	278	2.49	262		1.0x10-10	5.97	13.5	2,029,000#
5. <u>Six Rings</u> Benzo(g,h,i)peryl en e	(A)	. 276	0.26	222		1.0x10-10	7.23		
1ndeno(1,2,3-Cd)pyrene		276	62	163		1.0x10-10	7.66		

Sims and Overcash (1983). [†]Karickhoff et al. (1979). [#]Means et al. (1980) (mean value is reported).

to trap the heavy oil residuals before discharging to a creek or to the publicly-owned treating works (POTW). Ponds ranged from less than an acre to eight acres. Normally the ponds were lined with the local soils. Typical constituents present in creosote wastewater are given in Table 9.

Normal wood-treatment operations create additional preservative waste. Treating tanks and cylinders have to be cleaned periodically to maintain quality standards. In the past these preservative sludges were used as fuel or for road paving or were buried at the facility.

Preservative-contaminated soil is another source of environmental concern. Treated material is withdrawn from the cylinder and moved by rails to storage areas. During transportation the preservative drips from the treated wood onto the soil along the track. The areas around storage, treating, and unloading tanks have had minor preservative spillage from broken pipes, bleeding of treated wood, etc. These areas can be rather large, especially in the older railroad and pole plants.

DECOMPOSITION/IMMOBILIZATION OF PCP AND CREOSOTE COMPONENTS IN SOIL Pentachlorophenol

A large number of studies on biodegradation of PCP in soil have been done. The sequence of reactions that have been shown to occur is summarized in Figure 2. In soil, PCP undergoes a reversible methylation reaction to form pentachloroanisole, but this reaction apparently is not part of the main decomposition pathway. The main route for decomposition is not through the methyl derivative, but through PCP

Creosote Component	Composition of	Allowable	Allowable Discharge ^a		
	Whole Creosote	1977	1983		
	Percent	Pound	s/day		
Naphthalene	3.0	5.0	1.4		
2-Methylnaphthalene	1.2	2.0	.6		
1-Methylnaphthalene	.9	1.5	. 4		
Biphenyl	. 8	1.3	. 4		
Dimethylnaphthalenes	2.0	3.4	1.0		
Acenaphthene	9.0	15.1	4.3		
Dibenzofuran	5.0	8.4	2.4		
Fluorene	10.0	16.8	4.8		
Methylfluorenes	3.0	5.0	1.4		
Phenanthrene	21.0	35.3	10.0		
Anthracene	2.0	3.4	1.0		
Carbazole	2.0	3.4	1.0		
Methylphenanthrenes	3.0	5.0	1.4		
Methylanthracenes	4.0	6.7	1.9		
Fluoranthene	10.0	16.8	4.8		
Pyrene	8.5	14.2	4.0		
Benzofluorenes	2.0	3.4	1.0		
Chrysene	3.0	5.0	1.4		

Table 9. Daily discharge of creosote wastewater pollutants by the woodpreserving industry (USDA 1980).

^a Discharges are based on a flow rate of 5,000 gal/day per plant, 90 plants, and discharge limitations on oil and grease of 45 mg/liter in 1977 and 13 mg/liter in 1983.



Figure 2. Proposed route for decomposition of pentachlorophenol.

(Kaufman, 1978; Matsunaka and Kuwatsuka, 1975). The route of decomposition involves dechlorination leading to a series of partial dechlorinated products, such as 2,3,5,6-tetrachlorophenol.

The second step in the decomposition reaction involves an oxidation step to form substituted hydroquinones or catechols, such as 2,3,4;5tetrachlorocatechol. The oxidation product then undergoes ring cleavage, ultimately forming CO_2 and an inorganic chloride ion.

Mobility, persistence, and fate of PCP in soils depend on physical and chemical characteristics of the soil as well as the prevailing microbial population.

Hilton and Yuen (1963) compared soil adsorption of PCP to the soil adsorption of a number of substituted urea herbicides. They found that the adsorption of PCP was the highest of all compounds studied.

Choi and Aomine (1972, 1974, 1974a) studied the interaction of PCP and soil in detail. Adsorption and/or precipitation of PCP occurred to some extent on all soils tested. Choi and Aomine (1974) concluded in a study of 13 soils that adsorption of PCP depended primarily on the pH of the system. The more acid the soil, the more complete was the "apparent adsorption" of PCP. Different mechanisms of adsorption dominate at different pH values. It should be noted that PCP is an acid which forms a salt at the higher pH's. In the salt form, PCP would be more soluble in water but also more polar. In acid clays "apparent adsorption" involved the adsorption on colloids, and precipitation in the micelle and in the external liquid phase. Organic matter content of soils is important to adsorption of PCP at all pH values. Soil containing humus always adsorbs more PCP than soil treated with H_2O_2 to remove organic matter. Later investigations led to the conclusion that adsorption of PCP by humus is important when the concentration is low, but at higher concentrations the inorganic fraction increases in importance.

Three of four allophanic soils showed a significant increase in PCP adsorption at higher temperatures, while the fourth soil showed a decrease (Choi and Aomine, 1974a). The difference between the three soils and the fourth soil could be explained by assuming that andosols chiefly adsorb PCP as anions; whereas, the major factor influencing PCP adsorption by the fourth soil, showing a decrease with increasing temperature, is due to Van der Waal's force. Decreasing the concentration of chlorides or sulfate ions also increases the adsorption of PCP to soil. These results indicate the occurrence of competition between inorganic anions and PCP anions for adsorption sites on the soil colloid.

The persistence of PCP in soil depends on a number of environmental factors. Young and Carroll (1951) noted that PCP degradation was optimum when the moisture content of soil was near saturation. Kuwatsuka and Igarashi (1975) reported that the degradation of PCP is faster under flooded conditions than under upland conditions. Loustalot and Ferrer (1950) found that the sodium salt of PCP was relatively stable in air-dried soils, persisted for 2 months in soil of medium moisture content, and for 1 month in water-saturated soil. Although the rates of degradation may be maximized at the higher moisture values, these conditions would not be suitable for land treatment because of the increased potential for migration.

There are several factors in soil which affect the persistence of PCP. PCP is broken down slower in heavy clay than in sandy or sandy clay soils (Loustalot and Ferrer, 1950). This could be due to factors in the soil or to a slower oxygen transfer in the soil. An extensive study of the soil variables affecting the rate of degradation of PCP was carried out by Kuwatsuka and Igarashi (1975). The rate was correlated with clay mineral composition, free iron content, phosphate adsorption coefficients and cation exchange capacity of the soil, while the greatest effect was correlated with organic matter. According to these authors, little or no correlation could be found with soil texture, clay content, degree of base saturation, soil pH, and available phosphorus.

The preponderance of information indicates that microbial activity plays an important part in the degradation of PCP in soil. PCP decays more rapidly when the ambient temperature approaches the optimum value for microbiological activity (Young and Carroll, 1951). Ide et al. (1972) found no decay in sterilized soil samples. These factors suggest that microorganisms play an important role in PCP degradation (Kuwatsuka and Igarashi, 1975; Young and Carroll, 1951). Kuwatsuka and Igarashi (1975) studied degradation of PCP in soils collected from flooded and upland areas. Upland soils degraded PCP more rapidly in the laboratory when studied in the aerated condition, while soils obtained from flood conditions degraded PCP more rapidly when tested in the flooded stage. Thus, PCP-degrading microorganisms present in the soil survived the transfer to the laboratory and were most active when placed in an environment to which they were adapted.

A summary of the literature values for the persistence of PCP in soil is presented in Table 10. The persistence ranged between 22 days and 5 years. The 5-year value obtained by Hetrick (1952) was from dry soil sealed in a jar and probably does not represent a realistic evaluation of the environmental half-life. Thus, PCP can be considered moderately persistent under most conditions.

Numerous degradation products have been isolated from PCP-treated soil. Ide et al. (1972) identified 2,3,4,5-, 2,3,5,6-, 2,3,4,6-tetrachlorophenol; 2,4,5- and 2,3,5-trichlorophenol; 3,4- and 3.5-dichlorophenol; and 3-chlorophenol. Similar products were obtained by Kuwatsuka and Igarashi (1975), who also identified pentachloroanisole as a PCP degradation product. This reaction is reversible and pentachloroanisole can subsequently degrade back to PCP. Demethylation and methylation of phenolic groups in biological systems are well known (Williams, 1959). Ide et al. (1972) found 2,3,4,5-, 2,3,5,6- and 2,3,4,6-tetrachloroanisoles; 2,3,5-trichloroanisole; 3,4- and 3,5-dichloroanisoles; and 3-chloroanisole as methylated products of PCP in incubated soil. Based on the results obtained from these investigations, Matsunaka and Kuwatsuka (1975) proposed the soil degradation pathway shown in Figure 2. An excellent review of the parameters important for degradation of pentachlorophenol in soil can be found in a review by Kaufman (1978).

Many types of bacteria and fungi are capable of degrading pentachlorophenol, including <u>Pseudomonas</u>, <u>Aspergillus</u>, <u>Trichoderma</u>, and <u>Flavobacterium</u>. Chu and Kirsch (1972) isolated a bacterial culture by continuous flow enrichment that was capable of metabolizing PCP as a sole source of organic carbon. The morphological and physiological

Degradation parameter	Soil type	Special conditions	Time
90% degradation	Arable layer in rice fields (ll soils)	60% water 25% water	Approx. 50 days Approx. 30 days
	Forest red- yellow soil sublayer	60% water 25% water	No degradation in 50 days
90% degradation	Wooster silt loam	7.5 kg/ha penta, optimum conditions for microbial growth	Approx. 22 days
Complete	Dry soil	Sealed in air- tight container	> 5 years
Effect on growth of corn and cucumbers	Fertile sandy loam	Air-dried Medium water Water saturated	> 2 months 2 months 1 month
90% degradation	Mature paddy soil	Low organic content	l month

Table 10. Degradation of pentachlorophenol in soil (USDA 1980).

Degradation parameter	Soil type	Special conditions	Time Approx. 72 days	
Complete degradation	Dunkirk silt loam	Aerated, aqueous soil suspension		
Complete degradation	Paddy soil	Soil perfusion	21 days	
Complete degradation	Warm, moist soil		> 12 months	
98% degradation	Permeable soil	Composted with sludge from wood-treating plant	205 days	

Table 10. (continued)

characteristics of the organisms suggest a relationship to the saprophytic coryneform bacteria. Chu and Kirsch (1973) established that the organism was responsive to enzyme induction with PCP as the inducer. Lesser induction occurred with 2,4,6-trichlorophenol. The degradation products resulting from the metabolism of PCP by this organism were not characterized.

Kirsch and Etzel (1973) derived a microbial population capable of rapid PCP degradation from a soil sample obtained on the grounds of a wood products manufacturer. When fully acclimated, the populations were dosed with 100 mg/liter of PCP and 68% of the PCP was degraded in 24 hours. These cultures were most effective when the PCP was the sole source of carbon.

Watanable (1973) reported penta degradation in soil samples perfused with 40 mg/liter PCP. Bacteria isolates capable of PCP decomposition were derived from a soil perfusion enrichment culture. Degradation and complete dechlorination occurred after 2 to 3 weeks of incubation. The bacterium was characterized as a <u>Pseudomonas</u> sp. or an organism from a closely related genus. Tetrachlorodihydroxyphenols and their monoethyl ethers were tentatively identified as a metabolic product of PCP by <u>Aspergillus</u> sp. (Cserjesi, 1972). A soil bacterium isolated by Suzuki and Nose (1971) was capable of degrading PCP. The major metabolites were pentachloroanisole and dimethyl ether; a minor metabolite was tetrachlorohydroquinone.

More recently Edgehill (Edgehill et al., 1984) isolated a soil bacterium capable of utilizing PCP as a sole source of carbon. The organism was a member of the coryneform group of bacteria, probably the genus Arthrobacter.

It is clear that bacteria and fungi capable of degrading PCP exist in nature. However, the number of species and their population may be limited. In most cases where rapid degradation of PCP by microorganisms has been demonstrated, the source of inoculum was from areas where PCP had been used for a long time.

Creosote Components

The major components of creosote are the polycyclic aromatic hydrocarbons (PAH's) with trace amounts of phenols and azaarenes. A wide range of soil organisms, including bacteria, fungi, cyanobacteria (blue-green algae), and eukaryotic algae, have been shown to have the enzymatic capacity to oxidize PAH's. Prokaryotic organisms, bacteria, and cyanobacteria use different biodegradation pathways than the eukaryotes, fungi, and algae, but all involve molecular oxygen.

Tausson (1950) first demonstrated that several PAH's, including naphthalene, anthracene, and phenanthrene, can serve as substrates for some soil organisms and are "completely" metabolized. Groenewegen and Stolp (1981) isolated microorganisms that can use the compounds mentioned above as their sole C source. However, they could show degradation of some of the less-water-soluble PAH's, such as benz(a)anthracene and benzo(a)pyrene (BaP), only when the PAH's were mixed with soil, water, and a substance to stimulate growth of oxygenase-active organisms. Shabad et al. (1971) discussed a number of experiments that demonstrated bacterial degradation of BaP in soil. They reported 50-80% destruction of BaP over a period of "several" days by bacteria in soil contaminated with shale oil containing high concentrations (up to 20,000 $\mu g/kg$) of BaP. Shabad et al. also found that the capacity of bacteria to degrade BaP increased with BaP content in the soil and that microflora of soil contaminated with BaP were more active in metabolizing BaP than those in "clean" soil. Cerniglia and Crow (1981) demonstrated the metabolism of naphthalene, biphenyl, and BaP by a number of different species of yeast, some of which were previously reported in high numbers in oil-polluted soils. Cerniglia and Gibson (1979) reported the degradation of BaP by a filamentous fungus, and Dodge and Gibson (1980) demonstrated the degradation of benz(a)anthracene by the same fungal species.

Cerniglia and Gibson (1979) reported that the metabolites formed during the degradation of BaP by a fungus were very similar to those formed during BaP metabolism in mammals. Such metabolites are probably responsible for the carcinogenicity of BaP. However, Shabad et al. (1971) reported that extracts of a medium containing BaP were less carcinogenic to mice (<u>Mus</u> spp.) after microbial degradation than before degradation. A more complete review of earlier research (before 1970) on microbial oxidation of PAH's was presented by Gibson (1972). Biochemical pathways for the degradation of a number of PAH's by soil microorganisms have been proposed by Fernley and Evans (1958), Evans et al. (1965) and Gibson et al. (1975). One proposed mechanism for the reaction is shown in Figure 3.

Generally, rates of degradation for PAH compounds decrease as the molecular weight increases; rates of degradation are faster in soil than water; and overall rates of degradation are faster where there is an acclimated bacteria population (Herbes et al., 1980). These observations had also been made earlier (Sims and Overcash, 1983).



Figure 3. Proposed mechanism for the microbiological degradation of anthracene (Rogoff 1961).

Compounds such as naphthalene, phenanthrene, and anthracene, which are readily metabolized, are relatively water soluble, while persistent PAH's, such as chrysene and benzo(a)pyrene, have a lower water solubility (Table 11). Exceptions exist with pyrene and fluoranthene in that these compounds are more soluble than anthracene and yet have not been found by some researchers (Groenewegen and Stolp, 1981) to be appreciably metabolized by soil microorganisms. Other factors that may affect the persistence of PAH compounds are insufficient bacterial membrane permeability to the compounds, lack of enzyme specificity and lack of aerobic conditions (Overcash and Pal, 1979).

Two sets of studies were recently completed by Bulman et al. (1985) to assess PAH loss from soil. In the first, a mixture containing levels of 5 and 50 mg/kg of eight PAH's [naphthalene, phenanthrene, anthracene. fluoranthene, pyrene, benzo(a)anthracene, chrysene and benzo(a)pyrene] was added to soil and the concentration of each compound was monitored with time. In the second experiment, 14C labeled benzo(a)pyrene and anthracene were added to unacclimated agriculture soil in biometer flasks. The distribution of 14 C as volatile, adsorbed, and degraded products was determined in sterilized and biologically active soil. In the first set of studies, naphthalene, phenanthrene, anthracene, pyrene, and fluoranthene disappeared rapidly from soil during an initial period of 200 days or less. A loss of 94 to 98 percent occurred during this period and approximated first-order kinetics, in some cases following a lag period. With the exception of anthracene, the first-order kinetic rate constants were the same for 5 and 50 mg kg^{-1} additions of PAH. Following the initial period, the remaining 2-6 percent of the added PAH

Substance	Initial Concentration (µg/g soil)	k (day ⁻¹)	1/2 Life (days)	Reference
Pheno1	500	0.693	1.0	Medvedev & Davidov (1972)
Phenol	500	0.315*	2.2*	Medvedev & Davidov (1972)
2,4-dimethylphenol	500	0.35-0.69	1-2	Medvedev & Davidov (1972)
4,6-dinitro-o-cresol		0.023	30	Versar, Inc. (1979)
2,4-dinitrophenol	5-50	0.025	28	Overcash et al. (1982)
2,4-dinitrophenol	20-25	0.099-0.23	3-7	Sudharkar-Barik & Sethunathan (1978)
4-nitrophenol		0.043	16	Verschuerer (1977)
Pentachlorophenol		0.018	28	Murthy et al. (1979)
Naphthalene	7	5.78	0.12	Herbes & Schwall (1978)
Naphthalene	7	0.005*	125*	Herbes & Schwall (1978)
Naphthalene	7	0.173	4+	Herbes & Schwall (1978)
Acenaphthylene	0.57	0.039	18	Sims (1982)
Acenaphthylene	57	0.035	20	Sims (1982)
Anthracene	0.041	0.019	36	Sims (1982)
Anthracene	41	0.017	42	Sims (1982)
Phenanthrene	2.1	0.027	26	Groenewegen and Stolp (1976)
Phenanthrene	25,000	0.277	2.5+	Sisler and Zobell (1947)
Benz(a)anthracene	0.12	0.046*	15.2*	Herbes & Schwall (1978)
Benz(a)anthracene	3.5	0.007	102	Groenewegen & Stolp (1976)
Benz(a)anthracene	20.8	0.003	231	Gardner et al. (1979)
Benz(a)anthracene	25.8	0.005	133	Gardner et al. (1979)
Benz(a)anthracene	17.2	0.008	199	Gardner et al. (1979)
Benz(a)anthracene	22.1	0.006	118	Gardner et al. (1979)
Benz(a)anthracene	42.6	0.003	252	Gardner et al. (1979)

Table 11. Kinetic parameters describing rates of degradation of PAH and phenolic compounds in soil systems (Sims and Overcash 1983, ERT 1985b).

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Substance	Initial Concentration (µg/g soil)	k (day ⁻¹)	1/2 Life (days)	Reference
Benz(a)anthracene	72.8	0.004	196	Gardner et al. (1979)
Benz(a)anthracene	0.07	0.005	134	Sims (1982)
Benz(a)anthracene	0.10	0.005	142	Sims (1982)
Benz(a)anthracene	0.15	0.005	154	Sims (1982)
Benz(a)anthracene	7	0.016	43	Sims (1982)
Fluoranthene	3.9	0.016	. 44	Groenewegen and Stolp (1976)
Fluoranthene	18.8	0.004	182	Gardner et al. (1979)
Fluoranthene	23.0	0.007	105	Gardner et al. (1979)
Fluoranthene	16.5	0.005	143	Gardner et al. (1979)
Fluoranthene	20.9	0.006	109	Gardner et al. (1979)
Fluoranthene	44.5	0.004	175	Gardner et al. (1979)
Fluoranthene	72.8	0.005	133	Gardner et al. (1979)
Pyrene	3.1	0.020	35	Groenewegen and Stolp (1976)
Pyrene	500	0.067	10.5	Medvedev and Davidov (1972)
Pyrene	5	0.231	3	Medvedev and Davidov (1972)
Chrysene	4.4	0	-	Groenewegen and Stolp (1976)
Chrysene	500	0.067	10.5	Medvedev and Davidov (1972)
Chrysene	5	0.126	5.5	Medvedev and Davidov (1972)
Benz(a)p yrene	0.048	0.014	50*	Herbes and Schwall (1978)
Benz(a)pyrene	0.01	0.001	694*	Herbes and Schwall (1978)
Benz(a)pyrene	3.4	0.012	57	Groenewegen and Stolp (1976)
Benz(a)pyrene	9.5	0.002	294	Gardner et al. (1979)
Benz(a)pyrene	12.3	0.005	147	Gardner et al. (1979)
Benz(a)pyrene	7.6	0.003	264	Gardner et al. (1979)
Benz(a)pyrene	17.0	0.002	420	Gardner et al. (1979)
Benz(a)pyrene	32.6	0.004	175	Gardner et al. (1979)

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Substance	Initial Concentration (µg/g soil)	k (day ⁻¹)	1/2 Life (days)	Reference
Benz(a)pyrene	1.0	0.347	2+	Shabad et al. (1971)
Benz(a)pyrene	0.515	0.347	2+	Shabad et al. (1971)
Benz(a)pyrene	0.00135	0.139	5+	Shabad et al. (1971)
Benz(a)pyrene	0.0094	0.002	406*	Shabad et al. (1971)
Benz(a)pyrene	0.545	0.011	66*	Shabad et al. (1971)
Benz(a)pyrene	28.5	0.019	37*	Shabad et al. (1971)
Benz(a)pyrene	29.2	0		Shabad et al. (1971)
Benz(a)pyrene	9,100	0.018	39+	Sims et al. (1987)
Benz(a)pyrene	19.5	0.099	7+	Sims et al. (1987)
Benz(a)pyrene	19.5	0.139	5+	Sims et al. (1987)
Benz(a)pyrene	19.5	0.231	3+	Sims et al. (1987)
Benz(a)pyrene	130.6	0.173	4+	Sims et al. (1987)
Benz(a)pyrene	130.6	0.116	6+	Sims et al. (1987)
Dibenz(a,h)anthracene	9,700	0.033	21+	Sims et al. (1987)
)ibenz(a,h)anthracene	25,000	0.039	18+	Sisler and Zobell (1947)

Table 11. (continued)

*Low temperature (<15°C) *High temperature (>25°C)

was lost at a much reduced rate, and the first-order rate constants tended to be higher with the 50 $mg \cdot kg^{-1}$ addition than the 5 $mg \cdot kg^{-1}$ addition of PAH.

Losses of only 22 to 88 percent were observed for benzo(a)anthracene, chrysene, and benzo(a)pyrene, and only one kinetic period was identified within the 400-day incubation period. With chrysene, the first-order kinetic rate constants were the same at the 5 and 50 mg·kg⁻¹ levels of addition; however, for benzo(a)anthracene and benzo(a)pyrene the rate constants differed. The disappearance of benzo(a)anthracene approximated first-order kinetics; however, a zeroorder kinetics was found for the disappearance of benzo(a)pyrene and chrysene.

The mechanisms of disappearance of anthracene and benzo(a)pyrene were assessed in a second set of studies using 14 C labeling. The results indicated that biological activity was responsible for some of the loss of anthracene from soil; however, binding to soil solids and volatilization (either as anthracene or as metabolites) were identified as the major loss mechanisms. Identification of loss mechanisms for benzo(a)pyrene was less successful due to the small amount of benzo(a)pyrene that disappeared during the incubation period. Binding of benzo(a)pyrene to soil solids appeared to be the major mechanism involved, while microbial transformation of the compound was minimal.

Tortensson and Stenstrom (1986) have cautioned, however, that an indirect measurement of mineralization such as liberated $^{14}CO_2$ from a ^{14}C -labeled compound may not always be reliable. They recommend that the rate of transformation of a substance be defined by direct

measurement of its disappearance. Liberation of labeled CO_2 may not be concurrent with transformation because transformed compounds may not be further degraded to labeled CO_2 during the time frame of the study.

Some PAH's with more than four rings are not known to be utilized as a sole carbon source but have been reported to be co-metabolized with other organic compounds. This process involves the concurrent metabolism of a compound that a microorganism is unable to use as a sole source of energy along with metabolism of a carbon source capable of sustaining growth. In a study by McKenna and Heath (1976), the co-metabolism of refractory PAH compounds in the presence of two- and three-ring PAH compounds was investigated. The degradation of pyrene, 3,4-benzpyrene, 1,2-benzanthracene, and 1,2,5,6-dibenzanthracene in the presence and in the absence of phenanthrene was measured. Separate cultures of Flavobacterium and Pseudomonas were maintained in the presence of each of the PAH compounds. Both Flavobacterium and Pseudomonas exhibited negligible utilization of the refractory PAH compounds in the absence of phenanthrene. However, Flavobacterium, in the presence of phenanthrene, was able to significantly degrade all four test compounds. Co-metabolism by <u>Pseudomonas</u> was not observed. In a similar experiment PAH compound degradation by a mixed culture was measured. For each PAH compound studied, one container of inoculum received naphthalene as a growth substrate while a second container received phenanthrene as a growth substrate. Cometabolism of pyrene. 1,2-benzanthracene, 3,4-benzpyrene, and 1,2,5,6-dibenzanthracene by the mixed culture was exhibited in the presence of either naphthalene or phenanthrene.

The fate of PAH compounds in terrestrial systems has been reviewed by Sims and Overcash (1983), Edwards (1983), and Cerniglia (1984). These reviews present additional information on PAH degradation.

The types of phenols present in creosote in general are more readily degraded than PAH's or PCP. The effect of phenols on soil microorganisms is dependent on the soil concentration or amount added (Overcash and Pal, 1979). At low doses (0.01-0.1 percent of soil weight), the phenol serves as an available substrate, and there is an increase in microbial numbers. As the dose level is increased (0.1-1.0 percent of soil weight), an increasingly strong inhibitory or sterilizing effect is noted. At these levels, a partial sterilization occurs in which there is a depression in microbial numbers, but not a complete die-off. After a period of time, microbes adapt or phenol is lost through sorptive inactivation or volatilization and a regrowth of population occurs.

BIOACCUMULATION/TOXICITY OF PCP AND CREOSOTE

Plant/Animal Uptake of PCP

Information on the uptake and translocation of PCP by plants is limited, and there is no information on the metabolism of PCP by plants. Jaworski (1955) found less than 0.01 mg/kg PCP in cottonseed oil of field-grown plants sprayed with 14 C-PCP. Similarly, Miller and Aboul-Ela (1969) could not detect PCP in cottonseed kernels of open bolls on sprayed plants. However, in contrast to Jaworski (1955), they found some translocation of PCP or a possible metabolite within the plants. PCP residues definitely existed in seed from bolls that were closed at the time of treatment. Miller and Aboul-Ela (1969) also observed the movement of ¹⁴C-labeled PCP in the first two leaves of cotton within 1 hour of treatment. After 8 hours, radioactivity was distributed through all the veins of treated leaves, but there was no movement of radioactivity out of the treated leaves even after 8 days.

Hilton et al. (1970) studied the distribution of radioactivity in sugar cane following either foliage or root application of ^{14}C -PCP. With leaf application, 100% of the radioactivity was found in the treated leaf after 2 weeks. After 8 weeks, 84% of the activity was in the treated leaf with minor amounts in all plant parts except roots. Root application was studied by growing plants in a nutrient solution containing ^{14}C -PCP for 4 weeks. Approximately 90% of the original radioactivity was recovered from the plants after 4 weeks, with over 99% found in the root system.

Uptake of PCP by animals can occur by inhalation, oral ingestion (including consumption of PCP-contaminated food and licking or chewing treated wood) and dermal absorption by direct contact with treated wood. There is some evidence that PCP may be a metabolic product of other environmental contaminants, but the significance of this source is not known. Koss and Koransky (1978) demonstrated the formation of PCP from hexachlorobenzene in rats, mice, hens, and trout. Hexachlorobenzene occurs widely in the environment, and low-level residues are frequently encountered in animal tissues. The rate of PCP formation from hexachlorobenzene is slow compared to the rate of PCP elimination. Thus, the levels of hexachlorobenzene encountered in tissues are not sufficient to account for the levels of PCP generally found.

Many phenols undergo conjugation reactions in animals (Williams, 1959). These reactions include the formation of glucuronides, ethereal sulphates, and monoesters of sulfuric acid. Some PCP is excreted unchanged, and the amount that is metabolized or conjugated depends on the species.

Approximately 40% of the 14 C-labeled PCP given to mice and rats was excreted unchanged in the urine (Ahlborg et al., 1974). 14 Ctetrachlorohydroquinone accounted for 5% of the excreted radioactivity in rats and 24% in mice. Larsen et al. (1972) found that 50% of the radioactivity of orally administered 14 C-PCP was excreted in the urine of rats in 24 hours and 68% was excreted in 10 days. Between 9 and 13% was excreted in the feces. Tissue analysis showed small amounts of 14 C activity in all tissues, with the highest level in liver, kidneys, and blood. In blood, 99% of the radioactivity was in the serum. A two-compartment urinary excretion pattern was proposed that had a 10-hour half-life for the first 2 days, followed by a 102-day half-life.

Braun et al. (1976) studied the pharmacokinetics and metabolism of PCP in rats and monkeys. Excretion of 14 C from the labeled PCP was mainly through the urine in both species. In the monkeys, only PCP was found; while in rats, PCP, tetrachlorohydroquinone, and the glucuronide conjugate of PCP were found. Residues were high in liver, kidneys, and blood, thus agreeing with Larsen et al. (1972). It was suggested that there was reversible binding of PCP to blood proteins. The half-life ranged from 13 to 17 hours in rats and from 72 to 84 hours in monkeys. This work failed to confirm the presence of the long half-life
compartment suggested by Larsen et al. (1972). The short half-lives of PCP suggest that there will be no buildup of residues to a toxic level with continuing intake of PCP.

Toxic Effects of PCP

The widespread use of PCP as an antimicrobial agent and the likelihood of commercial products being contaminated with certain highly toxic polychlorinated dibenzo-p-dioxins and dibenzofurans necessitate a review of the toxicological information currently available. Although this review is primarily concerned with data on PCP per se, available data on commercial samples are included for comparative purposes.

Oral Toxicity--The LD_{50} for PCP in male rats has been reported as 78 mg/kg (Deichmann et al., 1942), 90 mg/kg (Gabrilevskaya and Laskina, 1964), 146 mg/kg and 205 mg/kg, the last being Dowicide EC-7 (USDA, 1980). For the female rat, it was 135 mg/kg (Dow Chemical Co. Summary, 1969) and 175 mg/kg (EC-7) (Gaines, 1969).

The LD₅₀ for mice was reported as $130 \pm 9.5 \text{ mg/kg}$ (Pleskova and Bencze, 1959); for rabbits, 100-130 mg/kg (Deichmann et al., 1942); for guinea pigs, 250 mg/kg (Gabrilevskaya and Laskina, 1964); and for swine, 120 mg/kg (Harrison, 1959). Dreisbach (1963) has estimated an LD₅₀ dose for man to be as low as 29 mg/kg.

These data suggest that PCP has moderate acute oral toxicity, but that the LD_{50} value may vary with the quality and quantity of contaminants. Man appears to be more susceptible than the rodent and the female to be more susceptible than the male.

Skin Absorption--When PCP in an organic solvent was applied to rabbit skin under occlusion for 24 hours, 200 mg/kg was lethal, but 100 mg/kg and 50mg/kg were not (Dow 1969). The LD_{50} for rats has been reported as 96 mg/kg, 105 mg/kg, and 320 mg/kg (Demidenko, 1966; Noakes and Sanderson, 1969; Gaines, 1969) and that for mice as 261 \pm 39 mg/kg (Pleskova and Bencze, 1959).

Subcutaneous Injection--The LD_{50} for rats was 100 mg/kg, for rabbits 70 mg/kg (5% in olive oil) (Deichmann et al., 1942), and for mice 63 + 3.2 mg/kg (Pleskova and Bencze, 1959).

Intravenous Injection--The lowest dose of PCP reported to kill rabbits was 22 mg/kg (Kehoe et al., 1939) when it was instilled as a 1% aqueous sodium pentachlorophenate.

Inhalation--Exposure to 5 mg/l dust for one hour did not kill male and female rats (Reichhold Chemicals, 1974). Demidenko (1969) reported the LD_{50} by inhalation to be 225 mg/kg for rats and 355 mg/kg for mice. The exposure concentration and the calculations to arrive at the LD_{50} dose were not given in the abstract. Workers have reported that the dust is irritating to the mucous membrane of the nose and throat.

Irritancy Tests--Rabbit eyes exposed to solid material showed slight conjunctival and slight iritic congestion. Exposure of rabbit skin under occlusion caused minimal irritation on intact skin and slightly more on abraded skin (Dow, 1969).

Commercial samples have produced chloracne in the rabbit ear bioassay; whereas, the purified material has not. Positive reactions have been produced by topical or oral application (Johnson et al., 1973). Allergic contact dermatitis has not been a problem in handling the chemical.

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Mutagenic-Cytotoxic Potential--PCP has not shown mutagenic activity in the Ames test (Anderson et al., 1972), the host-mediated assay (Buselmaier et al., 1973), or the sex-linked lethal test on drosophila (Vogel and Chandler. 1974).

Teratogenic and Embryotoxic Potential--PCP did not cause deformities, but it was highly embryolethal and embryotoxic following oral administration to rats of 15, 30, or 50 mg/kg per day on days 6-15 of gestation. No effects were produced at 5 mg/kg (Schwetz and Gehring, 1973; Schwetz et al., 1974). Purified PCP, with its low nonphenolic content, was slightly more toxic than the commercial grade (Schwetz et al., 1974).

Oral administration of PCP to golden Syrian hamsters at levels ranging from 1.25 to 20 mg/kg daily from days 5 to 10 of gestation resulted in fetal deaths and/or resorptions in three of six test groups. PCP was found in the blood and fat of the fetuses (Hinkle, 1973).

Pregnant rats (Charles River-CD Strain) were given 60 mg/kg of labeled PCP on days 8 through 13 of gestation and were sacrificed on the 20th day. Only a small amount of PCP crossed the placental barrier and only slight teratogenic effects were noted (Larsen et al., 1975).

One of the concerns in use of technical grade PCP is the presence of trace contaminants including the chlorinated dioxins and furans. Limited toxicity data on two of the dioxins present in technical grade PCP--hexachlorodibenzo-p-dioxin and octachlorodibenzo-p-dioxin--are given in Table 12.

Compound	LD-50	Teratogenic Effect ^b	Embryo Toxicity ^b	Acnegenic Effect ^b
	mg/kg Body wt.	mg/kg/day	mg/kg/day	mg/liter
2,7-Dichlorodi- benzo-p-dioxin	1,000	None	None	None
2,3,7.8-Tetrachloro- dibenzo-p-dioxin	0.0006	0.001	0.00003	0.00004
Hexachlorodibenzo- <u>p</u> - dioxin	100	0.1	0.0001	0.01
Octachlorodibenzo-p- dioxin	1,000	None	100	None

Table 12. Toxicity of various dioxin isomers to experimental animals.^a

^a Source: Modified from Alliot, 1975.

^b Values denote the lowest dosage or concentration which gives rise to the corresponding effect.

Plant/Animal Uptake of Creosote

There is very little information on bioaccumulation/toxicity of creosote (Brown et al., 1984). The limited information on plant/animal uptake has recently been reviewed by the USDA (1980). There is considerably more information on the bioaccumulation/toxicity of the individual PAH's found in creosote. Edwards (1983), in a comprehensive review of PAH's in the terrestrial environment, summarizes the sources and fate of these compounds in the environment. His conclusions regarding the uptake, translocation, and metabolism in vegetation were

- Some terrestrial plants can take up PAH's through their roots and/or leaves and translocate them to various other plant parts.
- Uptake rates are dependent on PAH concentrations, solubility, phase (vapor or particulate), molecular size, support media anchoring the plants, and plant species.
- PAH's may concentrate in certain plant parts more than in other parts.
- Some PAH's can be catabolized by plants.

The health effects of the major PAH constituents in creosote are summarized in Table 13.

	Compound	Effect
1.	Unsubstituted 6-membered aromatic ri	ng systems
	$\int \int \int \int d$	
	chrysene 🗸 🗸	mutagenic initiator, carcinogenic
	pyrene	co-carcinogen [with fluoranthene benzo(a)pyrene], mutagenic
	benzo(a)pyrene	mutagenic carcinogenic, fetotoxic, teratogenic
	benzo(e)pyrene	carcinogenic, mutagenic
	benzc(a)anthracene	mutagenic, carcinogenic
	benzo(a)phenanthrene	initiator, mutagenic
	naphthalene	inhibitor
	phenanthrene	initiator, mutagenic
	anthracene	mutagenic
	dibenzanthracene	mutagenic
	acenaphthene	mutagenic
	triphenylene	mutagenic

Table 13. Health effects of chemical constituents of creosote (U.S. EPA 1984).

2. Unsubstituted aromatic ring systems containing 5-numbered rings



fluoranthene

benz(j)fluoranthene

co-carcinogenic, initiator, mutagenic carcinogenic, mutagenic

fluorene

mutagenic



	Compound	Effect
6.	Hydroxy compounds	
	phenol p-cresol o-cresol m-cresol	promoter promoter promoter promoter
7.	Aromatic amines	
		H ₂
	2-naphthylamine p-toluidine o-toluidine 2,4-xylidine 2,5-xylidine	carcinogenic carcinogenic carcinogenic carcinogenic carcinogenic
8.	Paraffins and naphthenes	
	[-CH ₂ -] n	(n is large, e.g., greater than 15)

No effects found in the literature for this structural class.

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APPENDIX B

SUPPLEMENTARY MATERIAL FOR FIELD EXPERIENCE WITH THE KPEG REAGENT Alfred Kornel, EPA-RREL, Cincinnati, OH

CHEMICAL DESTRUCTION/DETOXIFICATION OF CHLORINATED DIOXINS IN SOILS

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ABSTRACT

Laboratory experiments using 1,2,3,4 tetrachlorodibenzo-p-dioxin show that chlorinated dioxins in soil may be chemically reduced to levels below one part per billion. The decontamination processes involve the addition to the soil of a mixture of alkali metal hydroxide, polyethylene glycols or capped polyethylene glycols, dimethyl sulfoxide and water. The reagent is either added directly to the soil with mixing (in-situ process) or mixed 1:1 by volume with soil in an external reactor (slurry process). The dioxin is dechlorinated to a water soluble form, which may be then removed from the soil (slurry process) or allowed to biodegrade (in-situ process).

INTRODUCTION

The contamination of large areas of soil with dioxin have created a need for a cleanup method which is capable of handling large volumes of contaminated soil in a cost effective manner. Proposed treatment methods include incineration, solvent extraction and direct chemical dechlorination. This paper will discuss the successful use of direct chemical dechlorination in decontamination of dioxin contaminated soils on a laboratory scale and the implications of these data for large scale soil treatment.

The basis for use of chemical dechlorination as a decontamination method lies in the relationship between the toxicity of chlorinated dioxins and the number of chlorine atoms on the dioxin molecule. In order for a dioxin isomer to exhibit high toxicity a minimum of three chlorine atoms are required, and these must be in the 2,3, and 7 positions (1). In addition, the lipophilic nature of many chlorinated dioxins contributes to their bioaccumulation activity. The dechlorination processes used in this study reduce the number of chlorine atoms on the dioxin molecule and produce a hydrophilic material which is more easily removed from the soil than the parent dioxin.

PURPOSE

The purpose of this project is to identify and evaluate at the laboratory level an effective chemical process for destruction/detoxification of chlorinated dioxins in soil.

APPROACH

Direct chemical decontamination of soil can be considered to be a two step process;

1. Application of the reagent to the dioxin contaminated soil

2. Reaction of the dioxin and reagent

These two aspects of the process interact. For example, a reagent with high mobility in soil requires a less rigorous application method than a reagent which is highly viscous. However at a minimum the reagent must be capable of reducing dioxin concentrations to <1 ppb. or favorable mobility and ease of application become irrelevant. For this reason, the reaction system was selected first, with the method of application designed around the reagent system.

Application methods for direct decontamination of soil must be compatible with the reaction system selected. In order for a direct chemical " reaction process to be effective, the contaminated soil and reagent must be brought into close contact. The degree of contact between soil and reagent may be increased by mechanical mixing, by addition of diluents and co-solvents to increase the reagent mobility, and by heating the soil/reagent mixture to reduce the viscosity of the reagent. After selection of the reaction system, a variety of application methods were tested under laboratory conditions for use in dioxin soil decontamination.

In order to reduce the costs of handling and analyzing soil samples. a low toxicity dioxin isomer. 1.2.3.4 tetrachloro-p-dibenzo dioxin (TCDD), was used in place of 2.3.7.8 TCDD for all testing. Laboratory tests of 2.3.7.8 TCDD and 1.2.3.4 TCDD indicated that rates of reaction for the two isomers were sufficiently similar to allow generalization of results between isomers.

To insure sample uniformity, all samples for treatment used uncontaminated soil which was spiked with a known amount of dioxin. Each soil sample was spiked individually, with the entire sample used for analysis. Uncontaminated soil samples were obtained from the vicinity of a dioxin site in Mississippi and spiked with 1,2,3,4 TCDD before processing. Soil from an authentic test site was used to avoid the wide variations seen in previous tests of treatability of different PCB contaminated soils. It was anticipated that dioxin contaminated soils would show similar variations.

PROBLEMS ENCOUNTERED

Major problems encountered during

this project involved the analytical procedure. Analysis of soil samples by gas chromatography was frustrated by the large number of interferences found in the test site soils. The interference problem was exacerbated by the ability of the reagents used to extract materials from the soil which were not extracted by the analytical solvents used. While this high extraction efficiency for the treatment solvents contributed to the success of the dioxin destruction. it complicated the analysis. The failure of cleanup procedures to produce an acceptable sample necessitated a move to gas chromatography/mass spectroscopy as the primary method of analysts.

An additional problem was caused by the tendency of the test site soil to solidify if exposed to high temperatures (100°C or above) under alkaline conditions. This problem was solved by moving to lower temperatures, which proved adequate for purposes of treatment.

RESULTS AND DISCUSSION

Selection of Reagent System - Of the available reactions. including ultraviolet dechlorination, ruthenium tetroxide oxidation and nucleophilic substitution. nucleophilic substitution using alkali metal hydroxides has given the best results in both literature studies and laboratory trials. The preferred reactions of this type for use with halogenated aromatics involve combination of potassium hydroxide and polyethylene glycols to form an alkoxide, which is the reactive species. The addition of a sulfoxide catalyst/co-solvent. usually dimethyl sulfoxide. greatly enhances the rate and degree of reaction, although it is not known if this is due to the effectiveness of the sulfoxide as an extractant for aromatics or to the catalytic effect of the sulfoxide for substitution reactions. The probable mechanism for this class of reactions follows;

ROH + KOH ----- > ROK + HOH

Sulfoxide ArCl_n + ROK ------ > ArCl_{n-1}OR + KCL The partially dechlorinated, water soluble reaction product may continue to undergo dechlorination, depending on the reaction conditions. Several reactions of this type have demonstrated reduction of dioxin concentrations in liquids to <1 ppb.

Selection of Application Method - A wide variety of hydroxide/alcohol/sulfoxide reaction systems will effectively dechlorinate dioxins in liquid solution. However, application of the reagent to the soil in such a manner as to allow these reactions to occur is a significant problem. The necessary degree of contact has been achieved using two different approaches; direct addition of reagent or a reagent/water mixture to the soil with mixing in place (in-situ process) and excavation of the soil followed by mixing equal volumes of soil and reagent in an external reactor (slurry process).

Both the slurry and in-situ processes may be used at elevated temperatures. Heating methods for an in-situ system would use radio frequency (RF) or microwave heating(2). The simplest method of heating for the slurry process is to preheat the reagent prior to mixing of the soil and reagent. Both of these heating methods are applicable to large scale processing.

The two application methods have different areas of application. The in-situ process is limited to areas of shallow contamination and the soil and reagent may be mixed with conventional agricultural equipment. In addition, the degree of contamination must be relatively uniform. If small areas of high concentration or "hot spots", are present, the high local concentration of contaminant might exhaust the amount of reagent which may be economically applied. While the concentrations of dioxin generally observed in the field are not high enough to cause a problem, dioxins are often found in combination with other chlorinated wastes, which may be present in high concentrations. However, in suitable cases, large areas of shallow soil contamination could be treated in a fairly short period of time using the in-situ process. In cases where dioxin has penetrated to depths > 1-2 feet, or where significant areas of

high concentrations occur, the slurry process is more suitable. The slurry process, which uses large volumes of reagent followed by reagent recovery, is more suited to treatment of "hot spots" than is the in-situ process.

Results of Combined Application/ Reaction Process - The slurry and in-situ process results will be discussed separately.

Results of In-situ Processing - Two different reagents have been used for in-situ processing in this study; potassium hydroxide/polyethylene glycol 400/ dimethyl sulfoxide (KOH/PEG/DMSO) and potassium hydroxide/2-(2-methoxy ethoxy ethanol)/dimethyl sulfoxide (KOH/MEE/DMSO). Water has been added in some cases as a co-solvent in an attempt to give readier penetration of small amounts of reagent into the soil. Each set of samples had an associated set of spikes and blanks. The spikes used reagent without the addition of KOH and were handled in the same manner as the samples. The blanks were untreated soil. Samples treated at above ambient temperatures were maintained uncovered in a water bath unless otherwise noted. The results of the in-situ processing are summarized in table 1.

Discussion of In-situ Processing

Soike Recovery - The recovery of TCDD from solkes in the in-situ process was extremely variable, ranging from 120% to <4%. In general, the higher the temperature and longer the hold time, the lower the spike recovery. Sealing the top of the spike reduced the loss of TCDD for the 2 day KOH/MEE/DMSO run to less than that for the 1 day run, indicating that the lower spike recoveries are probably due to losses from volatilization and/or extraction into the spike solvent (PEG/DMSO or MEE/DMSO), which is not analyzed. In the slurry tests, where volatilization is not a factor, analysis of the spike reagent showed that some 77% of the original TCDD was present in the spike reagent. The highest spike recovery was from the 20°C run, which is consistent with the volatilization hypothesis. Extraction of the TCDD into a polar solvent would tend

Table 1 - Summary of Results	of In-situ	Processing	- A11 so	ils initial	ly at 2000 ppb
	wtz	temp,	time.	avg pp	b TCDD
	in soil	^O C	days	spi	spike
I:1:1 KOH/PEG/DMS0	20	20	7	980	2500
1:1:1 KOH/PEG/DMS0	20	70	7	<1	740
1:1:1 KOH/PEG/DMS0	20	70	1	5.3	730
2:2:2:1 KOH/MEE/DMSO/WATER	20	70	1	3.3	500
2:2:2:1 KOH/MEE/DMSO/WATER	20	70	2	2.8	870*
2:2:2:1 KOH/MEE/DMSO/WATER	20	70	4	2.1	210
2:2:2:1 KOH/MEE/DMSO/WATER	20	70	7	1.2	190
2:2:2:6 KOH/MEE/DMSO/WATER	20	70	7	2.1	140
2:2:2:30 KOH/MEE/OMSO/WATER	50	70	7	18	170
2:2:2:30 KOH/MEE/OMSO/WATER	20	70	7	50	70
BLANKS - ALL * SPIKES SEALED				<1	

to enhance volatilization, similar to the effects of water on the volatilization of PCBs in soil (3). It is interesting to note that the worst spike recoveries were in the MEE reagents which used water as a co-solvent.

Effects of Temperature - Only two reaction temperatures have been tested to date using the in-situ process. The improvement in reaction efficiency in going from 20°C to 70°C was dramatic, improving reaction efficiency from 50% to > 90%.

Effects of Reagent Formulation - BEG vs. HEE - The test results for the 70°C reactions were slightly better at 1 day for the MEE reagent and slightly better at 7 days for the PEG reagent. This difference does not appear to be significant.

Effects of Water as a Co-Solvent - Four sets of tests were run for 7 days at 70°C using KOH/MEE/DMSO with water as a cosolvent. These data show a good correlation between wt% reagent and TCDD concentration after 7 days, as shown in figure 1. The plot of % active reagent vs. ppb TCDD shows the expected first order relationship. This demonstrates that dilution of the reagent with water to provide more contact. followed by evaporation of the water to encourage reaction, was not effective in

reducing the amount of reagent required.

The plot of % reagent vs. ppb TCDD shows the expected first order relationship. This demonstrates that dilution of the reagent with water to provide more contact, followed by evaporation of the water to encourage reaction, was not effective in reducing the amount of reagent required.

Results of Slurry Processing - The slurry process conditions tested and the results of GC/MS analysis are summarized in table 2.

As little as 2 hours at 70°C were adequate to reduce TCDD levels from 2000 ppb to < 1 ppb, for a removal efficiency of > 99.95%. The bulk of this removal occurred in the first 30 minutes, when < 99% of the TCDD had been reacted. The reaction at 25°C was slower, but did remove 98% of the original dioxin after two hours.

Reagent Recovery Efficiency - Reagent recovery of the PEG reagents by distillation was only partially successful (about 50% recovery), due to the poor heat stability and low vapor pressure of the PEG. Reagent recovery by washing has been more successful, with 94-99+% recovery of reagent. The degree of recovery is important



Table 2 - Results of Slurry Processing

Reagent	Temp, ^O C	Rxn time, hrs	ppb TC00
1:1:1 KOH/PEG/DMSO	180-260	4	< 1
1:1:1 KOH/PEG/DMSO	180	2	< 1
1:1:1 KOH/MEE/DMSO	150	2	< 1
1:1:1 KOH/MEE/DMSO	70	2	< 1
1:1:1 KOH/MEE/DMSO	70	0.5	15
1:1:1 KOH/MEE/DMSO	25	2	36

Blanks - all < 1 ppb TCDD

Spikes - % recovery in soil - 0.1-5.9 - % recovery in decanted solvent - 77

to the overall economics of the process.

Dioxin Recovery Efficiency - Analysis of the PEG/DASO reagent used in the slurry process spikes gave a high recovery of dioxin (77%). As in the case of the insitu samples, slurry spikes were treated with an alcohol/sulfoxide mixture without the addition of alkali. Additional analysis of both the solvents and the soil (soil extracted with acetone/hexane after decantation of the alcohol/sulfoxide) from the slurry spikes showed the presence of a large variety of halogenated materials which were not originally added to the soil or removed from the soil using the analytical reagents. The amount of additional chlorinated material removed from the untreated soil by the PEG/DMSO was on the order of 140 ppm, calculated as lindane. These materials may be pesticide residues or naturally occurring chlorinated species. Analysis of treated slurry samples also shows these materials, although at much lower levels, indicating that these are some form of aromatic halide. Results of analyses for DDT, DDE and chlorinated dioxin were negative.

These data indicate that conventional methods of extraction may underestimate concentrations of halogenated organics in soil due to an inability to remove halogenated species from the humics present in the soil. while reagents containing PEG/DMSO are capable of removing these halogenated organices from treated soil.

PRELIMINARY ECONOMIC EVALUATION

In order to provide a rough estimate of relative costs, two scenarios were constructed. In the first case, a 1 acre site 3 feet deep was to be treated using the in-situ process with radio frequency heating. Capital costs for this option are estimated at \$2,970,000 for a capacity of 27,600 tons/year of soil (4). In the second case, soil was to be excavated and placed in a 3 reactor slurry process system. Capital costs for this option are \$2,350,000 for a 40,000 ton/year capacity. Capital recovery costs for both processes assumed an interest rate of 14% over 5 years. Cost estimates for the two cases are shown in table 3.

Table 3 - Preliminary Economic Analysis of In-situ and Slurry Processes Cost. S/ton soil

Cost item	in-situ	slurry
Capital recovery setup and operatin reagent	31 65 200	17 54 20
Total costs	296	91

The major difference in costs between the two processes is in the cost of reagent. In the in-situ process, where reagent is not recovered, this cost is 67% of the total cost. For the slurry process, the operating costs assume a site that is reasonably easy to excavate. For cases where excavation is required to levels below the water table or in very rocky soil, this cost could increase greatly, although this would also be the case for landfill or incineration. In cases where excavation is difficult, the overall costs for the in-situ process may be lower than for the slurry process.

CONCLUSIONS

1. Dioxin concentrations in soil can be reduced from 2000 ppb to <1 ppb by mixing the soil with a combination of alkali metal hydroxide, alcohol and sulfoxide.

2. Mixing of the soil and reagent can be done effectively in two different ways; direct addition of reagent to inplace soil with one time mixing (in-situ process) or combination of soil and reagent in a reaction vessel with continuous mixing (slurry process).

3. Estimated costs for processing are in the range of \$100-\$300/ton soil.

ACKNOWLEDGEMENTS

This work was supported by the United States Environmental Protection Agency under the direction of Mr. C. Rogers and the United States Air Force Headquarters Engineering and Service Center with the assistance of Lt. E. Heyse under EPA contract 68-03-3219.

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"PREPRINT EXTENDED ABSTRACT" Presented Before the Division of Environmental Chemistry American Chemical Society New Orleans, Louisiana August 30-September 4, 1987

FIELD VALIDATION OF THE KPEG PROCESS TO DESTROY PCBs. PCDDs. NAD PCDFs IN CONTAMINATED WASTE

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The presence of highly toxic and persistent chemicals in liquids, soils, sediments, and sludges in abandoned waste sites pose a threat to both public health and the environment. Incineration is frequently used to destroy high hazards, however, when operated under less than optimum combustion conditions acutely hazardous products including PCDDs and PCDFs can be formed and emitted in the combustion products. Various biological, chemical, and physical methods have been tested and have been demonstrated to be effective in varying degrees to destory halo-organics of environmental importance.

The U. S. Environmental Protection Agency (EPA) has supported research intramurally and extramurally since 1980, to develop an alternative method for in-situ or on-site destruction of halogenated pollutants. Chemical reagents prepared from polyethylene glycols and potassium hydroxide (KPEGs) have been demonstrated under mild conditions (25°-140°C) to dehalogenate PCBs, PCDDs, and PCDFs to less than 1 ppb. The reaction mechanism is nucleophilic substitution at an aromatic carbon.

Bench scale studies have already established conditions for PCB destruction to less than 1 ppm and PCDDs and PCDFs to less than 1 ppb. Toxicological -2-

tests have established that arylpolyglycol by-products from KPEG reactions are non-toxic. The non-toxic property of the by-products may allow for delisting and on-site desposal of treated materials. In July and August 1986, a 2700 gallon KPEG was used in Butte. Montana on a wood preserving site and in Kent. Washington on a waste disposal site to successfully destroy PCDDs and PCDFs (120 ppb - 200 ppm) in 17000 gallons of liquid waste to non-detectable levels. A prototype reactor designed to treat both liquids and solids will be tested in 1987 on selected Superfund and Department of Defense sites. These field studies will validate or establish conditions in the prototype reactor for destruction of PCEs, PCDDs and PCDFs to acceptable levels required by the regulations. This presentation will review treatment data, regulations for treated materials, costs, and the potentials of KPEG process for the destruction of a variety of halogenated pollutants.

"PREPRINT EXTENDED ABSTRACT" Presented before the Division if Environmental Chemistry American Chemical Society New Orleans, August 30 - September 4, 1987

DECONTAMINATION OF A SMALL PCB SOIL SITE BY THE GALSON APEG PROCESS

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SITE BACKGROUND

Bengart & Memel, Inc. a wholesaler of non-ferrous scrap metals, was originally founded in 1950 in Bulfalo, New York. From the early 1950's through 1978 Bengart & Memel received and dismantled PCB (polychlorinated biphenyl) transformers and capacitors, inadvertently releasing PCB into the soil. In the mid-1970s, soil samples from the property were found to contain greater than 50 ppm of PCBs. The New York State Department of Environmental Conservation subsequently issued a Consent Order for remediation which required that the PCB concentration in the soil be reduced to below 50 parts per million.

INTRODUCTION

Galson Research, with the assistance of the US EPA, has developed a patented chemical process (Galson Terraclene-APEG) which dechlorinates PCBs and dioxins in soils and sludges. The technology has been proven successful under a variety of situations in laboratory and field studies. The successful APEG cleanup implemented at the Bengart & Memel site was a small scale version of the Terraclene process, utilizing 55 gallon drums as the reaction vessels.

The Terraclene-APEG process entails the addition of liquid reagents to contaminated soil and heating the mixture until the PCBs in the soil decompose to lower toxicity, water soluble materials. The reactions in this process are shown below.

$$\bigcirc - \bigcirc + \text{ROK} \xrightarrow{\text{DMSO}} \bigcirc - \bigcirc + \text{KCL} (2)$$

The reagent components used in the cleanup operation were dimethyl sulfoxide (DMSO), polyethylene glycol with an average molecular weight of 400 amu (PEG), triethylene glycol methyl ether and higher homologs (TMH), 45% aqueous potassium hydroxide (KOH) and water. The reagent formulation used was 2:2:4:7:5 PEG:TMH:DMSO:45% KOH:water. The excess water was added so that the reagent would be a single liquid phase rather than a 2 phase mixture.

Soil decontamination using the Terraclene-APEG process involves 5 basic steps;

- 1. Set up the vapor system & enclosure as applicable to the site.
- 2. Mix reagent and add to reaction drums.
- 3. Attach heaters, insulation, and vent lines to the reaction drums.
- 6. Allow drum contents to heat and react.
- 5. Obtain sample for analysis.
- 5. Neutralize (and deodorize if desired) the caustic soil .

Fifty-one drums of PCB contaminated soil were processed utilizing the drums as reaction vessels. The single phase liquid reagent was added to the soil drums until the soil surface was covered; the reagent amounted to ~20% of the weight of the soil. The cost of the reagent per drum was about \$60.00 without recycle or reuse. Electric drum heaters (15(4) W) were attached and the drums were heated to at least 100°C for 2-3 days without mixing and were allowed to cool for at least 12 hours before sampling.

The drives were sampled using a 30 Inch soil auger attached to a hand drill. Four cores with taken from each drum, one in the center, one close to the edge and two spaced between the center and edge in different parts of the drum. Soil was collected by digging as deep as possible with the auger and attempting to bring soil up from the bottom of the hole. In digging out a core, it was necessary to work around the large rocks in the drum. Rocks and metal pieces larger than 2 inches in diameter were not included. The soil from the cores was collected in a plastic bucket and mixed well with a trowel. Samples were collected from the bucket in wide mouth jars.

Samples were bottle extracted with methanol and hexane. Extracts were cleaned up by brief washing with concentrated sulfuric acid and analyzed by GC with electron capture detector. Each peak in the PCB chromatograms was treated as a separate compound and quantified individually so that an accurate estimate of PCB concentration could be obtained in spite of the disruption of the arockor pattern. The PCB concentration in all 51 of the drums was reduced to below 50 ppm, the required "clean" level. Selected data are presented in Table 1.

Table 1. Selected Results

description	ppm PCB before	ppm PCB after
highest initial conc.	195	26.9
second highest initial conc.	. 167	15.8
highest final conc. by GRC	110	32.7
lowest final conc.	102	7.3
second lowest final conc.	64	7.7

Final PCB concentrations were not correlated with initial concentrations or with f = 6 variation \$ \sharp "1 @ \$ \bar{I} 6 variation \$ \bar{E} "1 @ \$ \bar{E} "1 @ \$ \bar{E} 6 variation \$1 va

to the extreme inhomogeneity of the matrix and differences in permeability of the soil to the reagent.

The treated soil was extremely alkaline and had to be brought to a neutral pH (between 5 and 9) before re-introducing the soil into the environment. Mixing was required for the neutralization procedure because 'hot spots' of either concentrated acid or base were unacceptable. The treated soil was shoveled into drums containing dilute hydrochloric acid and stirred. The pH of the liquid was checked periodically and more acid or soil was added depending on the pH. The excess liquid was decanted from the soil as a required for disposal. (Although the NYSDEC approved the return of the neutralized soil to the site, the site owner decided to dispose of the soil in a local sanitary landfill.)

Sites with small amounts of contaminated soil could use this drum scale process as an alternative to incineration or landfill. For larger sites this process would become too labor intensive to compete economically with a multi-ton per batch slurry unit.

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"FREPRINT EXTENDED ABSTRACT' Presented Before the Division of Environmental Chemistry American Chemical Society

New Orleans, Louisiana

August 30-September 4, 1987

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LABORATORY STUDIES OF THE DEGRADATION OF TOXIC CHLORIHATED COMPOUNDS CONTAINED IN HAZARDOUS CHEHICAL WASTE HIXTURES AND CONTANINATED SOILS USING A POTASSIUM HYDROXIDE/POLYETHYLENE GYLCOL REAGENT

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Polyethylene glycol (PEG) apparently serves as a phase-transfer catalyst in the KOH-PEG dehalogenation reaction with halocarbons. The important feature which the polyethylene glycol-mediated dehalogenation reaction offers is that of a controlled process which occurs at relatively low temperatures, 70°-100°C. In contrast, more conventional dehalogenation processes using only solid caustic usually require substantially higher temperatures, and are often violent or even incontrollable processes. The rather remarkable catalytic effect of PEG in such dehalogenation reactions was initially observed by Kimura and Regen [J. Org. Chem. 47, 2493(1982), J. Org. Chem. 48, 195 (1983)], although phase-transfer catalysts have been known for some time iC. M. Starks et. al., "Phase Transfer Catalysis." Academic Press, N.Y., 1978). The studies of Kinura and Regen suggest that polymeric alkoxides and/or hydroxides are formed from the reaction of KOH or NaOH with the PEG. Experiments by these investigators, in which the efficacy of various FEG compounds for promoting the alkaline dehydrohalogenation of 2-bromooctane was assessed, indicated a strong dependence of the catalytic activity upon the number of repeating PEG units in the molecule. Of the PEG compounds which were assessed FEG 600, which would correspond to n = 13.2, or an average molecular weight of 600. appeared to be the most effective catalyst at a reaction temperature of \$0°C and a reaction time of 2 hours. Pentaethylene olycol was only slightly less effective. Virtually all of the investigations of KOH(NaOH)-PEG dehalogenation reactions which have been previously reported in the literature have been involved with pure compounds. It seems certain that the complex mixture of halocarbons and various ther compounds which would typically be present in an actual hazardous chamical vasce material will react with these reagents somewhat differently than pure nalogenated compounds. Accordingly, an extensive series of experiments were accomplished in the present program to assess the efficacy of KOH-PEG reagents for destruction of halogenated compounds in a variety of actual waste chemical and/or crocess mixtures.

A major portion of the present study was concerned with a waste chemical mixture which originated from a pentachlorophenol wood treatment facility located in fontana. This waste, which contained about 3.5% pentachlorophenol in a self-cleum oil base also contained parts-per-million concentrations of various self-chlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF). The hiboratory distinguity which were conducted using samples of this waste material entailed the chlowing:

1. The chemical waste sample was starred vigorously in its container in order to ax it and make the sample as homogeneous as possible. Four separate aliquits of the sample were then removed from the container and transferred to new, pre-cl-aned place sample bottles fitted with Teflon-lined lids. Two of the smaller diports. amounting to 0.123 gram each, were not treated with KPEG, but were reserved for direct analysis, in order to determine the concentrations of PCDD/PCDF in the original waste sample. One of the larger sample aliquots, amounting to 19.82 grams, was treated as described below.

2. To the 19.82 grams of the sample were added 1.09 grams of solid KOH. The sample vessel was then placed in a sand bath (inside a glove box), maintained at a temperature of 85° C, for a period of 30 minutes, while the contents of the bottle were stirred continuously. After 30 minutes had elapsed, the bottle was removed from the sand bath, capped, and allowed to cool to ambient temperature. An aliquot of the mixture was then removed for subsequent analysis in order to determine if the KOH treatment alone had any effect on the PCDD/PCDF in the sample.

3. A portion of the KPEG reagent, prepared by heating PEG-400 saturated with solid KOH pellets, was heated in a water bath at a temperature of 75°C for a period of 1 hour, with constant stirring during this period. At the end of this time, the solution appeared uniform.

4. While the KPEG reagent was still hot (75°C). 21.20 grams of it bere removed from the container and immediately transferred to the bottle containing the chemical waste sample to which KOH had been previously added. The sample bottle was then returned to the samd bath, maintained at a temperature of 70°C, and continuous stirring of the sample with a Teflon-coated stirring rod was begun.

5. At intervals of 15, 30, 45, 60, 90, 120 and 480 minutes following addition of the KPEG reagent to the waste sample, small aliquots of the treated sample were removed for analysis. Duplicate aliquots were removed at the indicated time intervals to demonstrate replicability. Immediately after each aliquot was removed, the KPEG reagent contained therein (and any reaction which was still occurring) was quenched by adding 4 mL of 50% H2SO4, so that the pH of the solution was adjusted to pH = 10-11. These aliquots were subsequently subjected to GC-MS analyses to determine the concentrations of PCDD and PCDF.

A second set of experiments identical to those just described, with the exception that the reaction temperature was maintained to 100°C, was also accomplished. Summaries of the results obtained in both sets of experiments under conditions which yielded optimum dechlorination of PCDD and PCDF are presented in Tables 1 and 2. These results indicate that KPEG treatment of this waste for a period of 45 minutes at 70°C results in essentially complete dechlorination (2 99%) of all PCDD and PCDF. Similar results were obtained within 15 minutes following KPEG treatment at 100°C.

The results of similar studies of other hazardous wastes containing PCBs. chlorinated benzenes and other chlorinated phenols will also be described.

TABLE 1. CONCENTRATIONS OF PCDD IN UNTREATED, KOH-TREATED, AND KPEG-TREATED PCP/OIL WASTE SAMPLES

Concentrations in Parts-Per-Billion

Cample No cription	2, 3, 7, 8- TCDD	Total Tetra- CDD	Total Penta- CDD	Total Hexa- CDD	Total Hepta- CDD	Total Octa- CDD
mreated 0114	29.0	455	885	3292	20.405	81,579
Treated Oil* XON only 85°/30 min	27.6	475	975	3548	19,969	38 ,597
Treated Oil** * 45 min/70*	ND (0.64)	ND (0.31)	ND (0.64)	HD (1.38)	5.82	ND (3,9)
Treated Oila - • 15 min/100°C	ND (0.86)	ND (1.25)	ND (2.09)	ND (3.36)	2.25	4.4

Average of results obtained from two separate analyses. Treat 2 with KOR followed by KPEG.

TABLE 2. CONCENTRATIONS OF PCDF IN UNTREATED, KOH-TREATED, AND KPEG-TREATED PCF/OIL SAMPLES

Concentrations in Parts-Per-Billion

ample Sestraption	2.J.7.8- 	Total Tetra- CDF	Total Penta- CDF	Total Hexa- CDF	Total Hepta- CDF	Total Octa- CDF
Streat d 011*	24.0	138	507	1768	5184	6138
Treated Oil* ROB only 251/30 min	21.8	117	452	3695	474ů	6370
reated Oila (Conv70*	ND (0.21)	1.59	ND (0.42)	2.82	4.61	ND (4.36)
livated Oal4 5 15 min/100%C	5.45	109	ND (0.60)	2.73	ND (0.91)	ND (3,15)

Average of results obtained from two separate analyses. Trained with KOF followed by KPEG.

"PREPRINT EXTENDED ABSTRACT" Presented Before the Division of Environmental Chemistry American Chemical Society New Drleans, Louisiana, August 30-September 4, 1987

A STUDY OF THIONATION AS A POSSIBLE DETOXIFICATION TECHNOLOGY

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and

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Hazardous waste sites in the United States contain a wide variety and concentration range of chemical contaminents. The variety of organic chemical structures encountered extend from simple aliphatics to condensed ring aromatics. The persistence of some hazardous waste chemicals is due in part to the inability of the environment to cleanse itself of these materials. Aromatic halocarbons are among the more toxic and persistent compounds found.

The simple conversion of halogenated organics to a non-halogenated hydrocarbon has been an elusive target for the environmental chemist. Many of the ordinary reactions found in the lexicon of the organic chemist that permit this conversion are not durable for application to an environmental setting and are not cost-effective. With the organic substrate varying from aliphatics to aromatics, it is hard to envision a reaction scheme leading to the desired dehalogenation. One possible answer to this need is the use of sulfur for nucleophilic displacement of the attached halide. The reaction between p-dichlorobenzene and sulfur in the presence of sodium carbonate has been shown to lead to displacement of chloride with the formation of an insoluble polymer (1). The only drawback was that this reaction apparently requires a significant energy of activation with normal operating temperatures of 300-350 degrees Fahrenheit. This reaction was reported to occur in the solid state leading to the displacement reaction below the melting points of either sulfur or the sodium carbonate. Polymer formation from this reaction has been exploited commercially in the synthesis of the Ryton fiber (2,3,4). When the products of this reaction are compared with starting materials from a toxicological viewpoint, a low molecular weight potentially toxic halocarbon has been converted to a nonvolatile nontoxic degradable polymer of essentially low toxicity.

APPENDIX C

SUPPLEMENTARY MATERIAL FOR IN-SITU BIODEGRADATION OF ORGANIC POLLUTANTS IN GROUNDWATER Dr. C. Herbert Ward, Rice University, Houston, Texas

BIORESTORATION OF AQUIFERS CONTAMINATED WITH ORGANIC COMPOUNDS

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I. INTRODUCTION

Ground water is a major source of drinking, industrial, and agricultural water in the U.S. and a limited resource. Therefore, contamination of ground water by anthropogenic activities is of dire concern.¹ Organic compounds can contaminate aquifers by inadvertent spills, improper waste disposal techniques, and agricultural practices.² The widespread distribution of organic chemicals in ground water and the resulting adverse health effects have prompted both the public and scientific community to examine the fate of this limited resource.⁴ A 1980 survey of the drinking waters from 39 communities using ground water indicated that 23% of the wells were contaminated with dichloroethylenes and other halogenated aliphatic compounds.³ Other industrial chemicals such as toluene and phthalate esters have also been detected in various surveys of ground water quality.

There are a number of techniques available to remediate ground water contaminated with organic compounds. These include physical containment, *in situ* treatment with chemicals or microbes, and withdrawal and treatment via various forms of physical, chemical, or biological processes.⁴ Examples of physical containment techniques are excavation and removal to a secure site, installation of barriers to ground water flow, and hydrodynamic control by injection and production wells. *In situ* chemical treatment involves inactivating or immobilizing contaminants with chemical agents. In addition to physical companies and *in situ* chemical treatment, subsurface pollutants can be treated *in situ* by stimulating the native microbial population. Another *in situ* biostimulation technique which has not yet been demonstrated is the inoculation of the subsurface with a microbial population that has specialized metabolic capabilities. Related processes such as the addition of bioemulsifiers or surfactants to increase the availability of subsurface contaminants to the microflora can also be used. Contaminated ground water can be withdrawn and treated by physical processes such as adsorption onto activated carbon or transfer to the gaseous phase by air stripping.

Reprinted from the CRC Critical Reviews in Environmental Control, Vol. 18, Issue 1, pages 29-89, 11988 by CRC Press, Inc.

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chemical processes such as precipitation, oxidation, or reduction reactions, or biological processes. Combinations of these processes are often more successful than individual techniques. When applicable, biological treatment may offer the advantage of partial or complete destruction of the contaminants rather than simply transferring the pollution to another phase of the environment.

II. IN SITU TREATMENTS

A. Microbial Activity in Aquifers

1. Evidence for Microbial Activity in the Subsurface

Technologies for *in situ* biorestoration of polluted aquifers have resulted from research indicating that subsurface microorganisms exist, are metabolically active, and often nutritionally diverse. Most of the research on ground water microbiology was initiated by a review, published in 1973, by Dunlap and McNabb⁵ of the Robert S. Kerr Environmental Research Laboratory, which addressed subsurface biological activity in relation to ground water pollution. Before publication of the review, the concept of biological activity below the rhizosphere had not been widely received. Microbiologists were skeptical about biological activity in the subsurface because of the oligotrophic conditions that exist below the rhizosphere⁶ and by an early study which indicated that microbial numbers decline precipitously with depth.⁷

2. Sampling Methods for Subsurface Microbes

A document that described sampling methods for subsurface microorganisms was published in 1977 by the Environmental Protection Agency (EPA).⁸ The method for procuring a representative sample of unconsolidated subsurface soil has since been modified.⁹ A soil sample is collected by first drilling a borehole to a desired depth with an auger and then taking the sample with a core barrel. After sample procurement, the core is extruded through a sterile paring device that removes the outer layer of soil that has come in contact with the core barrel. The remaining soil core is thus uncontaminated by the sampling procedure and is considered to be representative of the subsurface.

Investigations of microbial activity in the subsurface conducted prior to the development of the sampling techniques were equivocal because of the potential for contamination during sample procurement. In addition, many of the investigations were conducted using well water instead of core material. Recent evidence suggests that the majority of subsurface microorganisms is associated with soil particles.¹⁰ In addition, well water may contain microorganisms that are artifacts of the well because of subsurface contamination during well installation and changes in water quality around the well.

3. Microbial Numbers in the Subsurface

Methods to enumerate the subsurface microflora also have been developed. Electron microscopy, viable counts, epifluorescence microscopy, and measurements of biochemical components have been used to estimate microbial biomass.^{9,11-22} In contrast to Waksman's study,⁷ which reported that microbial numbers declined with depth, uniform population levels around 10⁶ to 10⁷ cells/g dry soil, measured by epifluorescence microscopy, were reported for profiles of uncontaminated shallow aquifers.^{9,11,12,16-18} However, bacteria in a chalk aquifer (consolidated) were sporadically distributed with depth.²³ Close examination of the subsurface strata indicated patchiness of bacterial populations; samples from the top of the unsaturated zone of an artesian aquifer yielded the highest counts, whereas those from bedrock and confining layers yielded the lowest total counts.²⁴

4. Microbial Ecology of the Subsurface

Bacteria are the predominant form of microorganism observed in the subsurface, although a few higher life forms have been detected.^{9,11,19} Some eukaryotic forms which may be

fungal spores or yeast cells have been observed in the upper 10 m of a soil profile.^{12,20,22} Bacteria, protozoa, and fungi have been detected in samples of ground water collected from 1-year-old wells.²⁵ In addition, a slow-growing amoeba has been isolated and cultured from the ground water interface of an uncontaminated soil.^{16,24}

Organic matter that enters the uncontaminated subsurface is usually the more refractory humic substances which resist degradation while percolating through the biologically active soil zone. The organic material available for metabolism by the subsurface microflora is likely to be present in low concentrations and difficult to degrade. The majority of microorganisms present in such nutrient-poor environments is generally oligotrophic. Characterization of the subsurface microflora indicates that the bacteria are usually smaller ($<1 \mu$ m in size) than those in eutrophic environments and both Gram-positive and -negative cell types are present.^{9,11,12} Gram-positive forms predominate in many uncontaminated soils. The predominance of small, coccoid cells, and hence a large surface-to-volume ratio for enhanced nutrient uptake, is a likely mechanism for survival in an oligotrophic environment such as the uncontaminated subsurface.⁹ In contrast, subsurface soil contaminated with creosote waste was found to contain more biomass and a greater proportion of Gram-negative to Gram-positive microbes when compared with uncontaminated soil from the same site.^{13,15}

5. Metabolic Activity of the Subsurface Microbial Community

Studies have also indicated that many subsurface microorganisms are metabolically active. Of the total cell count, about 0.01 to 50% can be recovered by plating on solid media and about 1 to 10% exhibit respiratory activity measured by the reduction of 2-(*p*-iodophenyl)-3-*p*-nitrophenyl)-5-phenyl tetrazolium chloride by cytochromes.^{16,18} Microbial activity, measured by the hydrolysis of fluorescein diacetate, declined with depth in the unsaturated zone of Ultisols and Alfisols.²² however, 2-(*p*-iodophenyl)-3-(*p*-nitrophenyl)-5-phenyl tetrazolium chloride reduction varied greatly between strata of a soil profile obtained from a shallow aquifer.²⁴

Many subsurface microorganisms are nutritionally diverse (Table 1). Simple substrates such as glucose, glutamic acid, arginine, a mixture of amino acids, and a synthetic compound, nitrilotriacetic acid, were mineralized in samples of uncontaminated ground water.²⁶ Polar solvents such as acetone, isopropanol, methanol, ethanol, and tert-butanol also have been reported to degrade aerobically by subsurface microorganisms.^{27,28} More challenging contaminants that are aerobically degraded by subsurface microorganisms include the methylated benzenes, chlorinated benzenes,²⁹ chlorinated phenols,³⁰ and methylene chloride.²⁷ Highly lipophilic compounds such as naphthalene, methylnapththalenes, dibenzofuran, fluorene, and phenanthrene are also biotransformed in the subsurface.^{11,32}

The microflora in some uncontaminated soils require little or no acclimation period to degrade many xenobiotics. For example, toluene, chlorobenzene, and bromodichloromethane were biotransformed in uncontaminated soil, but not 1.2-dichloroethane, 1.1.2-trichloroethane, trichloroethylene, and tetrachloroethylene.⁹ Benzene, toluene, and the xylene isomers were found to degrade in uncontaminated subsurface soils.³³ In addition, methanol (80 to 100 ppm) was degraded completely after 2 months, whereas tert-butanol degraded much slower in two uncontaminated anaerobic aquifers.³⁴

In contrast to reports of degradation of xenobiotics added to uncontaminated soil, long periods of acclimation to subsurface pollutants may be required before biodegradation can occur. Wilson et al.³¹ reported degradation of naphthalene, 1-methyl naphthalene, 2-methyl naphthalene, dibenzofuran, and fluorene at 100 to 1000 $\mu g/\ell$ in subsurface soil in the plume of contamination from a creosote waste pit; however, degradation of these compounds was not observed in uncontaminated soil from the same site. The time and concentration required for acclimation of the microflora to subsurface pollutants are unknown. Spain and van Veld³⁵ reported a threshold concentration of 10 ppb for adaptation to p-nitrophenol in samples of sediment and natural water. A better understanding of acclimation processes may explain

Table 1ORGANIC COMPOUNDS THAT HAVE BEENSHOWN TO BE BIODEGRADABLE IN THESUBSURFACE

Compound	Soil from con- taminated area	Aerobic	Ref.
Natural compounds			
Glucose	No	Yes	26
Glutamic acid			
Arginine			
Solvents	ν.	Nai	
Acetone	Yes	res	27
Ethanol			
Isopropanol		¥	30
tert-Butanol	Yes	tes	28
Methanol		N	0
Bromodichloromethane	NO	res	9
Aromatics		V	
Benzene	No	res	33
Xylene	.,	N	20
Methylated benzenes	Yes	Yes	29
Chlorinated benzenes		N/ -	•••
Chlorinated phenols	Yes	Yes	30
Naphthalene	Yes	Yes	31, 32
Dibenzofuran			
Fluorene			
Phenanthrene			
Toluene	No	Yes	9
Chlorobenzene			

why some chemicals persist in the subsurface even though they have been reported to degrade in laboratory cultures and samples of surface water and soil.

6. Environmental Factors Which May Limit Biodegradation

Environmental factors may limit or preclude the biodegradation of subsurface organic pollutants, even in the presence of adapted organisms. The recalcitrance of compounds thought to be biodegradable may result from a lack of an essential nutrient, substrate concentration, substrate inaccessibility, and the presence of toxicants.³⁶ Transport of contaminants in the subsurface also affects biodegradation. Transport is discussed in detail in Section IV.

Biodegradation of many organic pollutants in the subsurface may be limited by insufficient concentrations of oxygen. Alexander³⁷ reported that even the metabolism of carbohydrates may be inhibited in oxygen-depleted environments. Lee and Ward³² found that the rate and extent of biotransformation of naphthalene, 2-methyl naphthalene, dibenzofuran, fluorene, and phenanthrene were greater in oxygenated ground water than in oxygen-depleted water. Contrary to general theory that complete degradation (mineralization) of hydrocarbons requires molecular oxygen, more recent research suggests that alternate pathways exist under anaerobic conditions. Kuhn et al.³⁹ reported mineralization of xylenes in samples of river alluvium under denitrifying conditions. In addition, benzene, toluene, the xylenes, and other alkylbenzenes were metabolized in methanogenic river alluvium that had been contaminated with landfill leachate;⁴⁰ mineralization of toluene was confirmed by adding ¹⁴C-labeled toluene and measuring the amount of ¹⁴CO₂ produced. Grbic-Galic and Vogel³⁹ also reported mineralization of toluene and benzene under anaerobic conditions by a methanogenic consortium acclimated to ferulate. Further tests indicated that water supplied the oxygen that is first incorporated into the monoaromatic compounds.⁴⁰

The presence of oxygen may inhibit the biodegradation of many halogenated aliphatic compounds in the subsurface. Degradation of trihalomethanes, trichloroethylene, and tetrachloroethylene did not occur in aerobic cultures of sewage bacteria; however, the trihalomethanes were degraded anaerobically by mixed cultures of methanogens.⁴¹ In addition, Bouwer and McCarty⁴² reported that chloroform, carbon tetrachloride, and brominated trihalomethanes, but not chlorinated benzenes, ethylbenzene, or naphthalene, were biotransformed under denitrifying conditions.

In addition to oxygen, other nutrients may limit the biodegradation of organic pollutants in the subsurface. Inorganic nutrients, such as nitrogen and phosphorus, may be limiting when the ratios of carbon to nitrogen or phosphorus exceed that required for microbial processes. On the other hand, the presence of sulfate may inhibit methanogenic consortia that have been reported to dehalogenate and mineralize many chlorinated aromatic compounds.^{30,43}

The effect of substrate concentration on biodegradation of organic compounds in surface soils and waters has been documented.⁴⁴ Thresholds below which degradation is slow or does not occur may exist for compounds that are readily biodegradable at higher concentrations. Boethling and Alexander⁴⁵ reported that 10% of 2.4-dichlorophenoxyacetate at concentrations of 22 pg/m ℓ and 2.2 ng/m ℓ was mineralized in stream water, whereas about 80% was mineralized at higher concentrations of 0.22 and 22 µg/m ℓ . On the other hand, microorganisms may be inhibited or killed by high concentrations of organic pollutants that result from injection wells and hazardous waste sites. Lee⁴⁶ reported that glucose mineralization was inhibited in subsurface soil heavily contaminated with creosote; however, glucose was mineralized in uncontaminated and slightly contaminated core material from the same site.

Other factors such as sorption, pH, and temperature may also affect biodegradation of pollutants in the subsurface. Many of the organic compounds contaminating the subsurface are highly lipophilic. These compounds are sorbed by soil more strongly than the more hydrophilic compounds.⁴⁷ Sorption may enhance degradation by concentrating nutrients or. conversely, may prevent degradation by rendering the substrate unavailable to the microorganism. Zobell⁴⁸ reported that sorption of organic material to solid surfaces in dilute nutrient solutions increased microbial respiration. In contrast. Ogram et al.⁴⁹ observed that 2-4 dichlorophenoxy acetic acid sorbed to soil was completely protected from microbial degradation. Therefore, sorption may be important in nutrient scavenging in uncontaminated aquifers which are generally oligotrophic; however, sorption may compete with the micro-flora for subsurface pollutants that are relatively hydrophobic.

The soil pH may affect sorption of ionizable compounds in addition to limiting the types of microorganisms in the subsurface. Methanogens, which have been implicated in mineralization of some aromatic hydrocarbons, are inhibited at pH values less than 6.5^{50} Nitrification, the microbial conversion of ammonia to nitrate, is also limited at pH values below 6 and is negligible below 5. Hambrick et al.⁵¹ also reported that mineralization of octadecane and naphthalene in sediment was faster at a pH of 8 than 5.

Temperature also influences microbial metabolism of subsurface pollutants. The temperature of the upper 10 m of the subsurface may vary seasonably; however, that between 9 to 18 m approximates the mean air temperature (between 3 and 25°C in the U.S.) of a particular region.⁵² Biodegradation of subsurface pollutants in the more northern climates may therefore be limited by cooler temperatures. Bartholomew and Pfaender⁵³ reported that the microbial metabolism of m-cresol, nitrilotriacetic acid, and chlorinated benzenes in fresh water and estuarine areas decreased as temperature decreased. Atlas⁵⁴ and Mulkins-Phillips and Stewart⁵⁵ also reported a direct relationship between petroleum hydrocarbon degradation and temperature.

In summary, the subsurface environment contains microorganisms that degrade many of the organic compounds that contaminate ground water. The subsurface microflora in un-

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contaminated aquifers is probably oligotrophic. The majority of the microorganisms is associated with soil particles. Even in the presence of adapted populations, environmental factors such as temperature, pH, dissolved oxygen levels, inorganic nutrient concentrations, and the availability and concentration of the organic contaminants may limit biodegradation of subsurface pollutants.

B. Biostimulation by Addition of Limiting Nutrients

1. Development of the In Situ Biostimulation Process with Oxygen Supplied by Air Sparging a. Application of the Degradative Activity of Subsurface Microbes

The potential for biodegradation of organic compounds in contaminated aquifers was first recognized in 1971. Williams and Wilder⁵⁶ observed that ground water contaminated with gasoline from a leaking pipeline in the Los Angeles-Glendale, Calif., area contained bacteria that degraded hydrocarbons; however, studies indicated that biodegradation of the gasoline was limited by the availability of oxygen, mineral nutrients, and hydrocarbon surface area. These investigators suggested that the hydrocarbon-degrading bacteria could be used to clean the aquifer of residual gasoline; however, concern was expressed that bacterial growth would plug the well and formation during the process. McKee et al.⁵⁷ conducted bacteriological investigations using soil, water, and bacteria from the Los Angeles-Glendale, Calif., site and found several species of Pseudomonas and Arthrobacter that could degrade gasoline. The total number of gasoline-degrading bacteria in the ground water numbered over 50,000 cells/m ℓ in the contaminated zone, but less than 200 cells/m ℓ had been found in the uncontaminated wells and in wells where gasoline had not been detected for a year. The presence of high numbers of gasoline-degrading bacteria was suggested as an indicator of cleanup progress. Column studies designed to investigate the fate of gasoline trapped in the pore space of soil from the site indicated that the bacteria rapidly degraded the gasoline in the zone of aeration but slowly degraded that in the saturated zone. In a similar study, Litchfield and Clarks enumerated hydrocarbon-degrading bacteria in ground waters from 12 sites which were contaminated with petroleum. The numbers of hydrocarbon-degrading bacteria ranged from 10³ to 10⁶ cells/m², with similar numbers of both aerobic and microaerophilic organisms, in ground waters containing more than 10 ppm hydrocarbon. Hydrocarbon-degrading bacteria were found in ground water from all 12 sites; however, on a site-by-site basis, there were no relationships between the types of organisms, the type of petroleum contamination, the geological characteristics, or the geographical location of the site.

Application of the degradative capacity of subsurface microorganisms to restore gasolinecontaminated ground water was first demonstrated by Raymond. Jamison. Hudson, and coworkers at Suntech.⁵⁹ In 1974, Raymond⁶⁰ received a patent on a process designed to remove hydrocarbon contaminants from ground waters by stimulating the indigenous microbial population with nutrients and oxygen. The process involves circulating oxygen and nutrients through the aquifer using injection and production wells. Placement of the wells is dependent on the area of contamination and the porosity of the formation, but usually they are no closer than 100 ft apart. The nutrient amendment consists of nitrogen, phosphorus, and other inorganic salts, as required, at concentrations that range from 0.005 to 0.02% by weight: oxygen is supplied by sparging air into the ground water. The process is projected to require about 6 months to achieve degradation of 90% of the hydrocarbons provided that the growth rate of the microorganisms was 0.02 g/ ℓ per day. The numbers of bacterial cells are expected to return to ambient levels after terminating the addition of nutrients. Cleanup efficiencies are highest for ground water contaminated with <40 ppm gasoline.

b. First Application of the Biostimulation Process

The biostimulation process patented by Raymond was first demonstrated at the site of a pipeline leak in Ambler. Penn. An estimated 380,000 ℓ of high octane gasoline had leaked into a highly fractured dolomite outcrop underlaid by quartzite.⁶¹ The depth to the water
table ranged from 9.2 to 30.5 m in the 46 monitoring wells installed at the site. Before biorestoration was attempted, remedial action consisted of conventional pump and treat technologies. The gasoline was contained by continuously pumping water from wells located in the spill area. About 238,000 ℓ of the gasoline was recovered by physical methods; however, recovery was incomplete and approximately 119,000 ℓ of residual gasoline remained. The concentration of dissolved gasoline in the withdrawn ground water averaged <5 ppm. The time required for remediation of the aquifer using this pump and treat technique was estimated to be more than 100 years.

During the initial phases of remediation, problems in analyzing the concentration of residual hydrocarbons were encountered.⁶¹ These problems were later attributed to gasoline degradation by bacteria in the ground water. A program designed to investigate the potential for biodegradation of the gasoline by these organisms was then initiated. A laboratory study indicated that supplements of air, inorganic nitrogen, and phosphate salts could increase the numbers of hydrocarbon-degrading bacteria by 1000-fold.⁶² Small-scale field studies also indicated that nutrient additions would enhance the growth of bacteria that degrade hydrocarbons.⁶³ A full-scale program to stimulate biodegradation of the gasoline in the aquifer was then initiated.²² The nutrient amendment, which contained ammonium sulfate, disodium phosphate, and monosodium phosphate, was injected into the aquifer as a 30% concentrate by batch addition. Biodegradation of 1 ℓ of gasoline was estimated to require 44 g of nitrogen, 22 g of phosphorus, and 730 g of oxygen. Batch addition of the nutrients worked as well as continuous addition and was more cost-effective; however, high concentrations of nutrients could osmotically shock the microorganisms. Oxygen was supplied by sparging air into the wells using paint sprayer-type compressors and carborundum diffusers with a flow rate of 0.06 m^3 /min. As a result of the treatment, the bacterial population increased from about 103 to 107 cells/ml. High bacterial counts mirrored locations of high gasoline concentrations at the site.61

During the biostimulation program at the Ambler, Penn., site, 32 cultures of bacteria that actively metabolized gasoline were isolated and characterized.⁶⁴ The isolates included species of the genera *Nocardia*. *Micrococcus*. *Acinetobacter*. *Flavobacterium*, and *Pseudomonas*: some cultures could not be identified. The results of experiments that investigated the metabolic capabilities of the isolates suggested that the *Nocardia* cultures were largely responsible for the degradation of the aliphatic hydrocarbons, whereas those from the genus *Pseudomonas* degraded the aromatics. Gasoline was degraded by a mixed culture from ground water. However, individual components of gasoline such as branched paraffins, olefins, or cyclic alkanes did not support the growth of any isolate.

The bioreclamation program conducted by Suntech in Ambler, Penn., was reasonably successful. During the period of nutrient addition, the concentration of gasoline in the ground water did not decline; however gasoline could not be detected in ground water 10 months later.⁶² A 1000-fold increase in the numbers of total and hydrocarbon-degrading bacteria was observed in ground water from many wells.⁶¹ The waters from some wells exhibited foaming because of high microbial numbers and associated exopolysaccharides. Counts of microorganisms determined 1 year after the nutrient addition was terminated indicated that the microbial population had declined. Estimates based on the amount of nitrogen and phosphorus removed from the nutrient solution suggested that between 88,600 and 112,400 ℓ of gasoline were degraded. However, this estimate was not particularly accurate because some of the nutrients may have been adsorbed by the soil or lost from the biostimulation area by dilution. In addition, the estimates were based on discrete samples rather than composited samples. Large quantities of nutrients were used in this project; approximately 79 t of food-grade reagents were purchased.

c. Steps in the Biostimulation Process

The basic steps involved in an in situ biorestoration program are (1) site investigation.

(2) free product recovery, (3) microbial degradation enhancement study, (4) system design, (5) operation, and (6) monitoring.⁴ The first step in the process is to define the hydrogeology and the extent of contamination of the site. Important hydrogeologic characteristics include the direction and rate of ground water flow, the depths to the water table and to the contaminated zone, the specific yield of the aquifer, and the heterogeneity of the soil. In addition, hydraulic connections between aquifers, potential recharge and discharge areas. and fluctuations in the water table should be considered. The sustainable pumping rate must also be determined.^{65,66} These parameters can be determined by surveying the existing data for that site and region, reconnaissance by experienced hydrogeologists, geophysical surveys, excavation of test pits, and installation of boreholes and monitoring wells.⁶⁷ Low dissolved oxygen concentrations may indicate an active zone of hydrocarbon biodegradation.⁴⁸ The types and concentrations of contaminants are also important.⁴⁶ The type of remedial action chosen for a particular site depends on the time elapsed since the spill, the areal extent of contamination, the nature of contaminants, and whether the contamination is acute, chronic, or periodic. The urgency for action and the treatment level that must be achieved will depend on the potential for contamination of drinking water or agricultural water wells.

After defining the site hydrogeology, the next step is recovery of free product. Depending on the characteristics of the aquifer and contaminants. free product can account for as much as 91% of the spilled hydrocarbon.⁶⁶ The remaining hydrocarbon, which is sorbed to the soil and dissolved in the ground water, may account for 9 to 40% of the total hydrocarbon spilled; the majority is usually sorbed, however, the dissolved phase is the most difficult to treat. The pure product can be removed using physical recovery techniques which include (1) a single pump system that produces a mixture of hydrocarbon and water that must be separated, but requires minimal equipment and drilling; (2) a two-pump, two-well system which utilized one well to produce a water table gradient and a second well to recover the floating product; or (3) a single well with two pumps in which a lower pump produces a gradient and an upper pump collects the free product.⁴ Physical recovery often accounts for only 30 to 60% of the spilled hydrocarbon before yields decline.⁶⁹ Continued pumping of contaminated wells may contain a spill.

Prior to *in situ* treatment, a laboratory study is conducted to determine the nutrient requirements that will enable the indigenous microorganisms to efficiently degrade the contaminants.⁴ Kaufman⁷⁰ suggested that these laboratory studies can provide a reliable basis for field trials; however, the studies must be performed under conditions that simulate the field. For example, Kuhlmeier and Sunderland⁷¹ conducted a laboratory investigation of the unsaturated zone using samples saturated with ground water. Clearly, the results of their study do not represent the fate of the organics in the unsaturated zone. A chemical analysis of the ground water provides little information about the nutrient requirements of the microflora.⁷² However, the chemistry of the site will affect the nutrient availability by reacting with the phosphorus.⁷³ In addition, nutrients may sorb onto soils, especially silts and clays, and be unavailable to the microflora.

Laboratory studies conducted to determine appropriate nutrient formulations can be performed using a number of techniques. An increase in the number of total and hydrocarbondegrading bacteria has been used to identify limiting nutrients in a factorial experimental design.^{62,72} However, an increase in microbial numbers does not demonstrate that the substrate of interest is being metabolized. Batch culture techniques designed to measure the disappearance of the contaminant⁷⁴ and electrolytic respirometer studies designed to measure the uptake of oxygen also have been used.⁷⁵ Biotransformation studies which measure the disappearance of the contaminants or mineralization studies which indicate the complete destruction of the compound to carbon dioxide and water will confirm that the contaminants are being degraded. Controls to detect abiotic transformation of the pollutants and tests to detect toxic effects of the contaminants on the microflora should be included.⁷⁶



FIGURE 1. Typical schematic for aerobic subsurface biorestoration.¹²



FIGURE 2. Use of infiltration gallery for recirculation of water and nutrients in *in situ* biorestoration.

A system for injection of nutrients into the formation and circulation through the contaminated portion of the aquifer must be designed and constructed.⁴ The system usually includes injection and production wells and equipment for the addition and mixing of the nutrient solution.⁷⁷ A typical system is shown in Figure 1. Placement of injection and production wells may be restricted by the presence of physical structures. In addition, wells should be screened to accommodate seasonal fluctuations in the level of the water table. Air can be supplied with carborundum diffusers.⁶¹ by smaller diffusers constructed from a short piece of DuPont Viatio tubing,⁷² or by diffusers spaced along air lines buried in the injection lines.78 The size of the compressor and the number of diffusers are determined by the extent of contamination and the time allowed for treatment.⁷⁷ Nutrients also can be circulated using an infiltration gallery (Figure 2); this method provides an additional advantage of treating the residual gasoline that may be trapped in the pore spaces of the unsaturated zone.⁷⁰ Oxygen also can be supplied using hydrogen peroxide, ozone, or soil venting (see section on alternative oxygen sources). Well installation should be performed under the direction of a hydrogeologist to ensure adequate circulation of the ground water.⁴ Produced water can be recycled to recirculate unused nutrients, avoid disposal of potentially contaminated ground water, and avoid the need for makeup water.

Inorganic nutrients can be added to the subsurface once the system is constructed. Continuous injection of the nutrient solution is labor intensive but may be preferred to batch addition in some instances. Continuous addition of oxygen is recommended because the oxygen is likely to be a limiting factor in hydrocarbon degradation.

The performance of the system and proper distribution of the nutrients can be monitored

by measuring the organic, inorganic, and bacterial levels.⁴ Carbon dioxide levels are also an indicator of microbial activity in the formation.⁸⁰ Depending on the characteristics of the nutrients and soil, nutrients can be removed from solution by sorption onto soil.⁷³ For example, about 90% of the ammonium and phosphate and 70% of the hydrogen peroxide added to a sandy_soil with low calcium, magnesium, and iron was recovered. After passage of a nutrient solution through a column packed with a clay soil that had high calcium and magnesium but low iron and chloride levels, 100, 66, and 25% of the ammonium, phosphate, and hydrogen peroxide were recovered, respectively. However, after passage of a nutrient solution through a column packed with a clay soil high in calcium, magnesium, and chloride, but low in iron, 75, 100, and 15% of the ammonium, phosphate, and hydrogen peroxide, respectively, were recovered. Both soil and ground water samples should be collected and analyzed to fully evaluate the treatment effectiveness.⁶⁵ Raymond et al.⁶¹ reported that the most difficult problem in optimizing microbial growth in the Ambler reservoir was the distribution of nutrients because of the heterogeneity of the dolomite formation.

d. Additional Case Histories in Which Oxygen was Supplied by Air Sparging

In situ biorestoration has been largely used to treat gasoline spills and with reasonably good success. However, many of the reports on *in situ* biorestoration lack sufficient data to judge fully the overall effectiveness and costs associated with the process.

In a high-permeability sand aquifer contaminated with hydrocarbons in Millville, N.J., the *in situ* biorestoration program was successful in removing free product, but residual hydrocarbons were found at the last sampling period.⁷² The nutrient solution was transported through the formation at rates of 2.4 to 4.2 ft/day; aerated water was also injected, but the dissolved oxygen was rapidly consumed and did not increase in some of the main wells. However, analysis of core material collected from the aquifer indicated that the concentration of gasoline had not changed substantially during the biostimulation program. During the initial treatment process, inadequate dissolved oxygen levels led to the microbial formation of phenol; however, phenol levels declined as a result of additional aeration. A 10- to 1000-fold increase in the number of gasoline-utilizing bacteria was noted in the area with the highest gasoline levels. The cleanup met the state requirement for removal of the free gasoline and was subsequently stopped.

At a gasoline spill in La Grange, Ore.. 9 months of treatment by *in situ* biorestoration and a vapor elimination program succeeded in removing the free product and mitigating the vapor problems at two restaurants.⁷⁸ Biodegradation of the gasoline was enhanced by circulating well-aerated ground water amended with inorganic nutrients. After 7 months of treatment, the concentration of gasoline in soil ranged from 100 to 500 ppm and the average concentration of dissolved organic carbon in the ground water was 20 ppm. After an additional 3 months of treatment, the dissolved organic carbon levels in the ground water had decreased to <5 ppm in the majority of the samples.

Fumes released from a pipeline spill of gasoline temporarily closed an elementary school.*t A pumping well was used to maintain the water table below the foundation of the school and physical recovery was used to remove two thirds of the gasoline. An enhanced biodegradation program was initiated by circulating nutrients and oxygen through the formation for 6 months. After the cleanup, hydrocarbons could not be detected and the fumes that had threatened the school had been eliminated.

e. Minimum Hydrocarbon Concentrations Achievable by In Situ Biostimulation

The minimum concentration of hydrocarbon that can be achieved by *in situ* biorestoration is unknown and is most likely site specific. A natural gradient field test in a sandy Canadian aquifer required 434 days to reduce 1000 to 2400 ppb of benzene, toluene, and the xylene isomers below the detection limits (1 to 2 ppb) in the absence of added nutrients and oxygen.³³ The distribution of dissolved oxygen in the plume was heterogeneous and probably controlled the biodegradation of the aromatics.

Jensen et al.⁸² suggested that the indigenous microflora should be able to reduce the concentration of hydrocarbons below $1 \ \mu g/\ell$ when the initial hydrocarbon concentration is <10 mg/ ℓ and adequate quantities of nutrients and oxygen are supplied. The results of batch experiments using ground water from hydrocarbon-contaminated aquifers showed that the native microflora could generally reduce the concentrations of toluene, benzene, the xylenes, trimethylbenzene, naphthalene, methylnaphthalene, biphenyl, ethylnaphthalene, and dimethylnaphthalene from a range of 400 to 1100 $\mu g/\ell$ to <1 $\mu g/\ell$ within 1 week in the presence of oxygen and nutrients; however, phenanthrene and toluene persisted at higher concentrations in two of the ground waters after incubation for 6 days.

The concentration of trace-level organics in an aquifer may be reduced by providing a primary substrate that supports microbial growth and allows the organisms to act upon the trace-level organics as secondary substrates.⁸³ The concentration of the trace organic or secondary substrate is thought to be below the minimum substrate concentration (S_{min}) required to support microbial growth.⁸⁴ The S_{min} concept was developed to describe limitations related to transport of organics into a biofilm and the subsequent kinetics of reaction. There are several examples of S_{min} . A reactor-fed laboratory-grade water containing 0.59 mg/ ℓ total organic carbon (TOC) was able to reduce acetate below the S_{min} value (0.03 mg ℓ) for acetate. Shimp and Pfaender⁸⁵ demonstrated that the addition of fatty acids, carbo-hydrates, and amino acids enhanced the ability of mixed microbial populations to degrade substituted phenols. These data suggest that the addition of naturally occurring substrates may enhance the biodegradation potential of some xenobiotics. However, the addition of a primary substrate may not support the removal of some compounds. A biofilm supported by thymine could utilize alanine and acetate, both common metabolites, but not phenol and galactose.⁸⁴

f. Combination of In Situ Biostimulation with Treatment Processes

In situ biorestoration has been successfully combined with other treatment processes to reduce organic contaminants in aquifers. In most cases, the contaminated ground water is withdrawn, treated by a physical, chemical, or biological above-ground treatment technique. and then recharged after aeration and addition of nutrients. The role of biorestoration in combination treatment schemes is often difficult to assess. Yaniga et al.⁸⁶ described the cleanup of a gasoline spill in which an air stripper was used to reduce the contaminants in the withdrawn ground water and to supply oxygen before the water was recirculated to the aquifer via an infiltration gallery. Before recirculation, ammonium chloride, sodium monophosphate, sodium diphosphate, iron sulfate, and manganese sulfate were added in slug batches to the treated water. Additional oxygen was supplied by sparging air into the wells. As a result, the dissolved oxygen increased from a range of 0-5 to 5-10 ppm: the hydrocarbon degrading bacteria increased from 10^2-10^3 to 10^3-10^4 cells/m ℓ with just oxygen addition by air stripping and sparging and then increased to 10° cells/mt with nutrient addition and additional oxygen. Brown et al.⁸⁷ identified another gasoline-contaminated aquifer which was treated using air sparging. An estimated 95,000 to 114,000 ℓ of gasoline entered a 6.1-m thick coarse grain sand and fine gravel aguifer. Recovery of free product accounted for 70,000 ℓ of the spilled gasoline; however, an estimated 38,000 ℓ was sorbed to the soil at concentrations of 2000 to 3000 ppm, and 30 to 40 ppm was dissolved in the ground water. The concentration of gasoline was reduced to <50 ppm in the soil and less than 1 ppm in the ground water by air sparging. Only 1 to 2 ppm of dissolved oxygen could be achieved in the wells by air sparging.

Ground water contaminated by a spill of four solvents— methylene chloride, n-butanol, acetone, and dimethylaniline— into a glacial till aquifer was withdrawn and treated by an activated sludge process. After the sludge settled, the treated ground water was recirculated into the subsurface through injection trenches after being aerated and amended with nutrients.²⁷ The recharge water contained organisms acclimated to the solvents in addition to

a nutrient amendment containing nitrogen, phosphate, magnesium, sulfate, carbonate, manganese, and iron. Additional oxygen was supplied to the aquifer using a series of injection wells. Removal efficiencies of methylene chloride, n-butanol, and acetone were >97% and the dimethylaniline levels were reduced by >93% in the above-ground treatment. The concentrations of the solvents in the resulting effluent decreased to 0.04 mg/ ℓ for n-butanol. 0.92 mg/ ℓ for methylene chloride, 0.18 mg/ ℓ for dimethylaniline, and 1.12 mg/ ℓ for acetone from initial concentrations of 19.1, 58.5, 2.9, and 38.8 mg/ ℓ , respectively. Based upon chemical oxygen demand (COD) and gas chromatography analysis, the plume was reduced in size by 90% after 3 years of operation.** The COD was reduced from 300 to 20 mg/(in one monitoring well. Based on the rate of ground water flow, this reduction in COD coincided with the expected arrival time of the treated ground water at that well. Elevated levels of carbon dioxide in ground water collected from the treatment zones, in comparison to those observed in uncontaminated and decontaminated wells, suggested that in situ biorestoration was occurring. However, the solvents were detected in the ground water beyond the projected date for completion of the project and the New Jersey Department of Environmental Protection standards had not been achieved after 3 years of operation.

Flathman et al.²⁵ and Quince et al.³⁸ discussed cleanup of a methylene chloride spill using physical and biological above-ground treatment processes and in situ biological treatment. Following sand filtration to remove particulates, air stripping combined with a heat exchanger to improve stripping efficiency was initially used to treat the withdrawn ground water: the water was used then to flush the soil.** Air stripping removed about 98 to 99.9% of the methylene chloride in the withdrawn water. The concentration of methylene chloride in the ground water in one downstream monitoring well was reduced by 97%. Enhancement of biodegradation by ammonia and phosphate amendments was used to further reduce the concentration of the methylene chloride. An activated sludge unit was seeded with acclimated organisms from a wastewater treatment plant receiving methylene chloride and these organisms were used to inoculate the soil.75 After 43 days of in situ biological treatment, the concentration of methylene chloride in ground water from a monitoring well 6 m from the spill declined from 192 to 6 ppm, and 156 ppm chloride was released; however, it could not be determined whether the added bacteria or indigenous microflora or both were involved in methylene chloride degradation. Both air stripping and biological treatment removed 99.9% of the initial amount of methylene chloride during the 4 months of field operation. The concentration of methylene chloride was reduced from 20,000 to <1 ppm in the source wells.88

The subsurface at the Naval Air Engineering Center in Lakehurst, N.J., was contaminated with ethylene glycol that resulted from the loss of about 4000 gal of cooling water from a lined surface storage lagoon.⁷⁶ The unsaturated zone was contaminated with concentrations of ethylene glycol as high as 4900 mg/kg soil, whereas the concentration of ethylene glycol in the ground water was 2100 mg/t. The highly contaminated soils were treated using injection and recovery wells, whereas the ground water contaminated with ethylene glycol was treated by an above-ground activated sludge unit and by adding ethylene glycol-degrading bacteria and nutrients to the subsurface. A biofeasibility study using an electolytic respirometer had demonstrated that the concentration of ethylene glycol could be reduced to <50 ppm within 10 days by the natural microflora in the ground water and that the concentration of ethylene glycol at 1300 ppm was not toxic. The initial operational phase was designed to degrade as much of the ethylene glycol as possible by treatment above ground with an activated sludge unit. The effluent from the activated sludge unit was amended with oxygen, nitrogen, and phosphorus, adjusted to neutral pH, and then reinjected into the subsurface to create a closed-loop system. The amended effluent was used to flush the contaminated soil and inoculate the ground water with nutrients and acclimated bacteria. The concentration of ethylene glycol in ground water collected from the plume recovery wells was reduced from 420 to 690 ppm to <50 ppm within 26 days;** however, the unsaturated zone still

contained pockets of ethylene glycol. A passive treatment system which involved adding lime and diammonium phosphate to the soil surface continued after termination of the active biorestoration phase. By the end of the treatment program, ethylene glycol could not be detected (detection limit, 50 ppm) in ground water collected from the production wells.

A shallow basin comprised of sand and pea gravel was contaminated with isopropanol and tetrahydrofuran.⁷⁴ In addition to isopropanol and tetrahydrofuran, acetone was also detected in the ground water and was believed to be a byproduct of isopropanol degradation. Remedial action consisted of a recovery system, treatment in an above-ground biological reactor, and recharge of the aguifer with the effluent from the reactor which created a closedloop system. The effluent, which contained acclimated bacteria, was also amended with nutrients before reinjection into the subsurface. The soils were flushed with the treated ground water to remove sorbed organics and introduce acclimated organisms into the aquifer. Maximum concentrations of isopropanol (950 ppm) and acetone (190 ppm) were detected in ground water from a centrally located well as a result of flushing pockets of contamination from the subsurface. The concentration of acetone in the ground water increased initially until the majority of the isopropanol had been degraded, and then it declined to <0.2 ppm. Extrapolations from the data indicated that 99% of the contaminants would be removed within 33 days. Estimated cost for removal and disposal of 5700 m³ of contaminated soil was \$550,000, whereas the biological treatment program was estimated to cost one fifth as much.

Winegardner and Quince³⁰ documented two case histories of *in situ* biorestoration that involved the addition of acclimated bacteria. The first case history described the cleanup of a semi-soluble aliphatic hydrocarbon plasticizer that was spilled during a train derailment. Recovery wells were used to collect the plasticizer from the subsurface. Later, surface recharge and shallow injection were used to flush the plasticizer out of the soil; the peak concentration of the plasticizer was >2000 ppm. This treatment reduced the areal extent of the contamination after 70 days, in addition to reducing the concentration of the plasticizer. Air stripping and carbon adsorption were used initially; however, these techniques were replaced by biological treatment using activated sludge. The water treated by the activated sludge contained bacteria that were acclimated to degrade the plasticizer and was injected into the subsurface to enhance *in situ* biorestoration. The concentration of the plasticizer in the water treated by the activated sludge was reduced from approximately 1700 to 400 ppm after clarification; however, the contribution of the activated sludge and *in situ* microflora in removal of the plasticizer in the treatment process could not be separated.

The second case history involved contamination of a glacial kame deposit of sand, gravel, silt, and clay with chloroform from a leaking pipeline. Ground water was withdrawn and treated with a mixed-media prefilter, an activated sludge bioreactor and settling vessel, and a heated air stripper. The effluent from the activated sludge bioreactor that contained bacteria acclimated to degrade chloroform was injected into the subsurface to enhance biorestoration. The effluent from the air stripper was discharged into a process sewer or into the subsurface. A forced flushing/recovery system was used to increase the recovery of the chloroform. Biological treatment followed the physical recovery; however, treatment effectiveness was not discussed.

2. Alternate Oxygen Sources

The supply of dissolved oxygen may limit in situ biorestoration of hydrocarbons, especially in low-permeability aquifers.⁷² Depending upon the temperature of the ground water, only 8 to 12 mg/ ℓ of dissolved oxygen can be achieved by air sparging, and incomplete transfer of oxygen into water may reduce this even further. Using only the oxygen provided by sparging air into the ground water, 1500 to 5400 pore volumes of air would be required to completely degrade the hydrocarbon in an aquifer that is 6 ft deep, 1 acre in size, has a porosity of 30%, and contains 4000 mg/ ℓ gasoline.⁹¹

Alternative sources of oxygen include pure oxygen, hydrogen peroxide, and ozone. Other methods of supplying oxygen to the subsurface are soil venting or air flooding⁹² and colloidal dispersions of air in a surfactant matrix.⁹³ Concentrations of 40 to 50 mg/ ℓ of dissolved oxygen can be achieved with pure oxygen; however, pure oxygen is somewhat expensive, may bubble out of solution before the microflora can use it, and may be an explosion hazard if handled improperly.⁹¹

a. Hydrogen Peroxide

Hydrogen peroxide, which decomposes to form one molecule of water and one half molecule of oxygen, also can be used as a source of oxygen (Equation 1).

$$H_2O_2 \to H_2O + 1/2O_2$$
 (1)

Hydrogen peroxide has great potential as an alternative source of oxygen but is toxic to microorganisms at species-specific concentrations. Before application of hydrogen peroxide to the subsurface, the tolerance range of the in situ microorganisms must be determined in a laboratory experiment. Concentrations of 3% are used as a sterilant and levels as low as 200 ppm can be toxic to microorganisms. Ground water organisms inoculated into sand columns could tolerate 0.05% hydrogen peroxide, but higher levels were toxic.⁴⁴ In a study. designed to investigate the effect of increasing concentrations of hydrogen peroxide on gasoline biodegradation, the culture acclimated to hydrogen peroxide levels that were gradually increased from 0.05 to 0.2%; however, removal of gasoline was not greatly increased in comparison to the control without hydrogen peroxide. Microbial counts were higher in columns in which hydrogen peroxide was incrementally increased than those which received only 0.05% hydrogen peroxide. These data suggest an oxygen limitation at lower concentrations of hydrogen peroxide. Large populations of microorganisms survived high hydrogen peroxide concentrations better than small populations.⁹⁵ In a study in which the oxygen concentration was varied from 8 to 200 ppm (using air. 60% nitrogen/40% oxygen, pure oxygen, or a hydrogen peroxide solution). microbial growth and gasoline degradation were greatest in columns amended with hydrogen peroxide, which provided the highest concentration of available oxygen.⁴¹ At concentrations >100 ppm, hydrogen peroxide may degas to form air bubbles which may block some of the pores in the aquifer. Decomposition of hydrogen peroxide may also be catalyzed by iron and fluctuations in pH.⁴⁴ In addition to comprising part of the nutrient formulation, certain forms of phosphate, such as potassium monophosphate, can be used to stabilize hydrogen peroxide solutions. To reduce phosphate adsorption by the soil, a combination of simple and complex polyphosphate salts can be used.⁹⁶ Results from a field test in which hydrogen peroxide was used to increase the dissolved oxygen content of the ground water indicated an increase from 1 to 15 ppm within 70 hr at a monitoring well located 7.6 m downgrade of the injection well.

Raymond et al.⁴⁷ received a patent on a process which involves stimulating biodegradation of organic contaminants in the subsurface with hydrogen peroxide. The patent described several formulations of nutrient and hydrogen peroxide solutions and processes that can stabilize the decomposition of hydrogen peroxide, control movement of the solution through the aquifer, remove metal ions from the subsurface which catalyze hydrogen peroxide decomposition, and disrupt biofilms that form agabe point of injection. Hydrogen peroxide decomposition can be controlled by the addition of peroxidase, oxidase, or a transition metal (iron, copper, manganese, chromium, or other material, including the chelated forms of these metals). In addition, condensed phosphates can be perfused into the aquifer to deactivate or remove substances that catalyze hydrogen peroxide decomposition.

Movement of the hydrogen peroxide solution through the formation can be controlled by hydratable polymeric materials, interface modifiers, and densifiers.⁹⁷ The hydratable polymeric materials, such as polysaccharides, polyacrylamides, and polyacrylamide copolymers.

increase the viscosity of the solution. An increase in viscosity reduces the rate of diffusion and slows the movement of the solution. The addition of surfactants will decrease the interfacial tension, prevent clays from swelling, disperse materials throughout the zone of contamination, and decrease the metal-catalyzed decomposition of hydrogen peroxide. For example, the zone of treatment can be extended into the capillary zone by adding soluble orthophosphoric salts and condensed phosphoric acids to increase the capillary rise of the aqueous solution. Salts, such as sodium chloride, calcium chloride, and sodium bromide, can be used to change the density of the nutrient solution. Biofouling can be controlled by adding high concentrations (0.5 to 3%) of hydrogen peroxide; the effectiveness of hydrogen peroxide in controlling biofouling may be enhanced by the addition of dilute acid.

Hydrogen peroxide has been used to enhance the oxygen supply in the subsurface in many remedial programs. In most cases, the additional oxygen was required to degrade hydrocarbons in aquifers contaminated from gasoline spills. One case study involved the contamination of a relatively impermeable soil (ground water movement, 0.6 to 0.9 m/year) with gasoline.⁶⁴ About 50 to 60% of the free product was recovered; however, concentrations of hydrocarbon in the range of 3700 to 7200 ppm remained sorbed to the soil. A feasibility study was conducted to identify an *in situ* microbial population capable of degrading the hydrocarbons when supplied with nutrients and oxygen. Hydrogen peroxide was used as the source of oxygen. After 2 months of operation, free product recovery reached a maximum of 95 to 114 ℓ/day , numbers of hydrocarbon-degrading bacteria increased one to three orders of magnitude, and the concentration of sorbed product declined to a range of 2300 to 2900 ppm.

In another in situ biorestoration program designed to clean up gasoline from a leaking underground storage tank, oxygen was initially supplied by air stripping and sparging and then by hydrogen peroxide. A layer of heavy silt loam which was underlaid by a layer of fractured shale and siltstone was contaminated by the spill.98 The gasoline infiltrated into the ground water and the resulting plume, containing dissolved hydrocarbons, contaminated 12 domestic water wells with concentrations ranging from <10 ppb to 15 ppm. Ground water was withdrawn and an air stripper was used to remove volatile organics and add oxygen: the oxygenated water was then recirculated into an infiltration gallery to facilitate removal of the trapped organics. Air stripping reduced the dissolved organics in the effluent to <0.1 ppm. Additional oxygen was introduced by sparging air through the 6.1- to 9.1-m water column in the wells. The initial dissolved oxygen levels in the contaminated zone were 0 to 1 mg/ ℓ , whereas those in the uncontaminated wells were 7 to 9 mg/ ℓ . Dissolved oxygen levels rapidly increased on the periphery of the plume; after 6 weeks of air sparging, the concentration of dissolved oxygen increased to 3 to 5 mg/ ℓ in the contaminated zone. The nutrient solution included ammonium chloride, sodium phosphate, and various mineral salts. Existing monitoring wells were used to add the nutrients because nutrient diffusion was slower than desired. In the first 20 months of treatment, the concentration of dissolved hydrocarbon was reduced by 50 to 85%, but treatment was continued because significant levels of hydrocarbon remained. After this treatment period, reduction in the concentration of dissolved hydrocarbon was minimal during the next 11 months and believed to be a result of inadequate oxygen supply;" in addition, a biofilm had developed and plugged the injection wells.**

To increase the concentration of dissolved oxygen, a triat experiment using hydrogen peroxide was conducted in which 18.9 ℓ of 100 ppm hydrogen peroxide was added to an injection well 12.2 m from a pumping well.⁴⁹ As a result, the dissolved oxygen content in the ground water collected from the pumping well increased from 0.5 to 8 ppm in 24 hr with a concomitant increase in microbial activity. Then 100 ppm hydrogen peroxide was added to the infiltration gallery and injection wells to increase the concentration of dissolved oxygen in the formation. Addition of hydrogen peroxide also controlled growth of the biofilm on the screens of the injection wells. After addition of hydrogen peroxide, the concentration

of hydrocarbons in the ground water had been reduced from 15 to 2.5 ppm. Continuation of this treatment removed the dissolved hydrocarbons in ground water from 8 of the 12 wells. Between 200 and 1200 ppb remained in the other four wells.⁹⁰

Hydrogen peroxide-assisted biodegradation followed by granular activated carbon (GAC) polishing was used to treat a spill of waste solvents and fuel. 79,100 The source of the contamination was an excavated area around several leaking tanks at a laboratory facility. The fill material and soil surrounding the storage tanks were contaminated with a mixture of hydrocarbons composed of xylenes, benzene, toluene, ethylbenzene, and C_4 - C_{12} alkanes that ranged in concentration from 1000 to 3000 ppm. About 2600 ℓ of free product was recovered using a sump pump; however, an estimated 1100 to 3400 ℓ of the hydrocarbon remained. The subsurface consisted of sand and sandy clay with fairly rapid ground water flows. The total number of bacteria in the well water ranged from 300.000 to 420.000 cells/mé; hydrocarbon degraders ranged from 5400 to 6100 cells/*ℓ*. Carbon adsorption and enhanced bioreclamation were considered for remedial action. Carbon adsorption was estimated to require 10 to 20 years and cost \$470,000 to \$850,000, whereas enhanced bioreclamation was estimated to require 4 to 8 months and cost \$180,000 to \$270,000.% Enhanced bioreclamation was chosen and the process design consisted of four injection wells and a pumping well with a flow rate of 57 to 95 *l*/min.¹⁰⁰ A nutrient solution consisting of ammonium chloride and sodium phosphates was injected by batch addition. Hydrogen peroxide was injected continuously following a short period during which only nutrients were added; addition of nutrients without oxygen had little effect because of the initial low dissolved oxygen content (0.8 ppm). After 72 days, 440 kg of nutrients and 945 ℓ of the hydrogen peroxide solution had been added. The number of hydrocarbon-degrading microorganisms increased 130-fold and the concentration of dissolved oxygen in the ground water increased to 10.5 ppm after the biorestoration program was initiated. The concentration of hydrocarbon decreased from 22,700 to 581 ppb in 44 days and to nondetectable levels in one monitoring well after 72 days. Elevated concentrations of contaminants detected in another monitoring well were thought to be a result of a leaking line. An estimated 570 to 1500 ℓ of the mixed fuels and solvents had been degraded.⁹⁶ However, the formation became partially clogged after 72 days of operation. Clogging of the formation may have resulted from the movement of silt and degradation of the cement that lined the storage tank vault.79 An activated carbon system was then used as a polishing step to reduce the hydrocarbon concentration below 10 ppb in the tank vault and soil.

The cost for a 6- to 18-month bioreclamation program at the laboratory facility was estimated between \$180,000 and \$270,000.⁴⁶ Estimates were \$50,000 to \$75,000 to start the bioreclamation process and \$130,000 to \$220,000 for services and nutrients. The cost for excavation was estimated between \$600,000 and \$1.5 million, and the program was projected to take less than 6 months; however, facilities on the site would restrict excavation. Withdrawal and treatment by carbon absorption was estimated to cost \$470,000 to \$850,000 and require 10 to 20 years because of limited extractability of the contaminants.

A less successful demonstration of enhanced bioreclamation using hydrogen peroxide was reported by Brown and Norris.¹⁰¹ A formation consisting of silt, sand, and gravel deposits was contaminated by a spill of 303,000 ℓ of unleaded gasoline. Two subsurface zones were identified in the test area: (1) a fine quartz sand with some limestone and dolomite grains and ferromagnesium minerals with traces of limonite and pebbles of dolomite, limestone, and granite and (2) another zone of fine quartz sand with large amounts of fines and silt which impeded ground water flow. The hydraulic conductivity ranged between 8.8 to 15.2×10^{-4} cm/sec. A free-product recovery program was implemented; however, between 300 and 10,000 ppm of hydrocarbon remained in the soil and 50 to 60 ppm remained in the ground water after 5 years. The concentration of total hydrocarbons in the cores averaged S477 ppm with a range of 4823 to 6331 ppm for several groups. The highest concentrations were detected at the water table at depths of 7.3 to 7.9 m. The treatment zone was estimated

to contain 6100 \pm 2500 (SD) kg of gasoline. Ambient nutrient levels in the ground water were <1 ppm and the dissolved oxygen content was <0.4 ppm. Total counts and counts of hydrocarbon-degrading bacteria grown on nutrient agar were 1.2×10^3 and 2×10^2 cells/g, respectively. Biostimulation was tested in a section of the plume surrounded by two triangular patterns of monitoring wells which surrounded an inner infiltration gallery. Nutrients were batch fed to the inner gallery and then followed by addition of hydrogen peroxide solutions which were gradually increased from 0 to 500 ppm. Phosphorus levels reached 100 to 250 ppm in the inner gallery and ranged from 1 to 10 ppm outside the gallery. The concentration of nitrogen ranged from 100 to 250 ppm in the inner gallery and from 10 to 50 ppm outside of the gallery. Total bacterial counts reached 10° cells/ml in the inner gallery and 6 × 10³ cells/ml outside of the gallery; the number of gasoline-utilizers also increased.

The concentration of hydrocarbon in the soil was measured after 0, 32, 91, and 164 days during the test and at depths of 7, 7.6, 8.2, and 8.8 m below the land surface.⁽⁰⁾ During the test, the concentration of hydrocarbon was reduced from 5490 to 1874 ppm (65%). Removal of hydrocarbons was highest (from 5643 to 1743 ppm) in the inner gallery near the injection area, whereas a low-permeability zone was less effectively treated because of reduced circulation of nutrients. In addition, the concentration of total hydrocarbons was reduced from 6087 to 4058 ppm and from 2946 to 1008 ppm immediately below the water table. The data indicate that substantial quantities of hydrocarbons remained adsorbed onto the soil after *in situ* biostimulation, although more improvement may have occurred with continued treatment.

A field demonstration of in situ biorestoration using hydrogen peroxide in a very gravelly clay loam was adversely affected by the low permeability $(3.9 \times 10^{-5} \text{ to } 3.3 \times 10^{-3} \text{ cm/}$ sec) of the soil.¹⁰² The heterogeneity of the soil and distribution of the contaminants made it difficult to inject nutrients and pump water. The contamination resulted from a disposal pit containing chromium sludges, electroplating wastes, chlorinated solvents, cresols, chlorobenzenes, and other compounds.^{103,104} The organic compounds that were identified included tetrachloroethylene, trichloroethylene, trans-1,2-dichloroethylene, and o- and p-dichlorobenzene. Heavy metals present at concentrations >10 mg/ ℓ included antimony, chromium. copper, lead, nickel, and zinc, and the concentrations of silver, cadium, and mercury were high in some locations.^{103,104} The formation consisted of gravel lenses and layers of finegrained soils with low hydraulic conductivities. The water table was perched, only 1.2 to 2.4 m thick, and exhibited seasonal fluctuations. Direct microbial counts in soil ranged from 7.6 to 170 \times 10° cells/g (wet weight); viable counts ranged from <100 to 7 \times 10° cells/ g on both rich and poor media. Laboratory studies conducted under aerobic conditions indicated that the chlorobenzenes, hydrocarbons, and aromatics could be biodegraded. The total resolved hydrocarbons, i.e., the organic contaminants separated by gas chromatography and thought to represent n-alkanes, were reduced more rapidly in the aerated microcosms than in those supplied with hydrogen peroxide, which may indicate hydrogen peroxide toxicity. Unresolved hydrocarbons representing branched alkanes were removed under aerobic but not anaerobic conditions. The results from these microcosm studies suggested that biological degradation was feasible, but the heterogeneity of the subsurface and the contaminants present seriously limited application of the biorestoration process. The presence of heavy metals was not expected to prevent biodegradation, but the treatment process could induce metal mobilization.

The treatment system design for *in situ* biorestoration consisted of nine extraction and four injection wells that were connected to a central surge tank and a distribution box.¹⁰⁵ One upgradient and two downgradient wells were installed to monitor the influence of the treatment in untargeted areas. Nutrients were added 2 weeks before the hydrogen peroxide. After 2 months of treatment, the effectiveness of the treatment could not be determined because of a change in analytical methods; however, a number of problems were noted with

the field demonstration. Hydrocarbon levels increased in the ground water for unknown reasons. In addition, the nutrient solution precipitated initially when added on a continuous basis; the precipitation problem was reduced by switching to batch amendments. The temperature in the well water increased and fluctuated because the impermeable soil could not sustain flow adequate to prevent the pumps from overheating. Microbial numbers in the infiltration zone remained low, perhaps due to hydrogen peroxide toxicity. Antimony and lead may have been mobilized within the aquifer and the nutrients had not reached most of the wells at the time of this report.¹⁰⁶

Continued treatment for 6 months resulted in decreases in the levels of chlorobenzene and total hydrocarbons.¹⁰⁷ The breakthrough of the nutrient solution was rapid in the highly permeable zones, but poor in the less permeable strata. Elevated concentrations of carbon dioxide were detected in the treatment zone which suggested an increase in microbial activity. However, the concentration of many of the organic compounds did not decline and biorestoration of the site was not successful.

b. Ozone

In addition to hydrogen peroxide, ozone (O_3) can be used as an alternate source of oxygen. Ozone was used in an in situ biorestoration program to remediate a hydrocarbon spill in a railroad yard in Karlsruhe. F.R.G.¹⁰⁸ The presence of organic contaminants in the drinking water wells for the city of Karlsruhe was traced to the hydrocarbon spill in the train yard. The concentration of organics, iron, and manganese in the ground water increased but the dissolved oxygen content decreased. The water was withdrawn, treated with 1 g of ozone per gram of dissolved organic carbon for 4 min and then reinjected into the formation through five infiltration wells at a rate of 80 to 120 m³/hr. Supplemental nutrients were not added. The purified water formed a barrier to prevent further contamination of the withdrawal well. The ozone treatment increased the dissolved oxygen levels in the ground water which stimulated the microbial population and enhanced the degradation of the contaminants in the aquifer. The maximum efficiency of introducing dissolved oxygen into the ground water was 80% of the initial concentration of ozone. Oxygen consumption by the indigenous microbes reached approximately 40 kg/day. The dissolved organic carbon decreased from a range of 2.5 to 5.5 g/m^3 to a steady-state value of slightly more than 1 g/m^3 ; few mineral oil hydrocarbons remained. The levels of iron and manganese were also reduced. Although the total number of bacterial cells increased, microbial counts on media which selected for disease-causing organisms did not increase. The removal of the hydrocarbons probably resulted from both in situ microbial activity and chemical oxidation by the ozone. Hydrocarbons could not be detected in the biostimulated section of the aquifer in water collected 1.5 years after treatment.

c. Soil Venting

Soil venting or air flooding can be used to supply oxygen for *in situ* biorestoration. Organic vapors from the unsaturated zone are removed by increasing the flow of soil gases using vapor recovery wells and air inlet wells.¹⁰⁹ The volatile organic contaminants partition into the soil gas and are transported to the vapor recovery wells. The increase in soil gas flow in the unsaturated zone makes more oxygen available to reaerate the ground water.

Field tests have demonstrated that soil venting is effective in removing hydrocarbons from the unsaturated zone. Following a gasoline spill in a porous and moderately permeable soil, the concentration of vapors was reduced by 90% at a distance of 6.1 m and by 70% at 12.2 m from the vacuum source.¹⁰⁰ After reequilibration for 2 weeks, the average concentration of the vapors was reduced to 38% of the pretest levels. Soil venting has also been used to remove from 10 to 15 kg of trichloroethylene per day in another field trial.¹¹⁰ A combination of vacuum extraction and withdrawal and treatment was able to reduce the levels of carbon tetrachloride by more than 99% in monitoring wells at a site contaminated by a storage tank spill.¹¹¹ After operation for 30 months, the concentration of carbon tetrachloride was reduced by 70% in the vadose zone. Levels of methane, acetone, and methylene chloride following another tank spill were reduced below explosive limits within 1 week. but 6 weeks were required to reduce the methylene chloride concentrations to drinking water standards.¹¹² Soil venting is restricted to volatile hydrocarbons in the unsaturated zone and, in some cases, the capillary fringe.¹⁰⁵ Formations with perched water tables or many types of contaminants may not be amenable to treatment by soil venting.¹¹⁰

Wilson and Ward⁹² suggested that air flooding can be used to supply oxygen during *in* situ biorestoration. Air contains 20 times more oxygen than water and is less viscous. For a fine sand or silt, about 32,000 pore volumes of water in comparison to 4000 volumes of air is required to meet the oxygen demand for degradation of saturating concentrations of hydrocarbons. Fewer volumes of each are required for more porous soils. In addition to supplying oxygen, air flooding also removes vapors by physical weathering. In the absence of a layer of pure product floating on the water table, the water table can be lowered by withdrawing ground water to bring the contaminated region into the unsaturated zone for treatment. However, lowering the water table would produce large quantities of contaminated ground water that must be treated. Soil venting is currently being applied for *in situ* restoration of gasoline-contaminated soil by supplying oxygen to a 30-m thick unsaturated zone where the contaminants are held.⁷¹

d. Collodial Gas Aphrons

Michelsen et al.⁹³ suggested that a colloidal dispersion of air contained in a surfactant matrix could be used to supply oxygen for *in situ* bioreclamation. The microdispersion of air, known as colloidal gas aphrons, is prepared by passing air or pure oxygen through a venturi with a very small gas entry port into a surfactant solution or by use of a spinning disk apparatus. The resulting colloidal material is basically a suspension of fine soap bubbles with diameters of 25 to 50 μ m that contain up to 65% gas. Up to about 55% of the pore space in sands can be filled with the colloidal air dispersion. Coarse sand was better than a fine sand in retaining the colloidal air. Laboratory tests indicate that the technique can support the aerobic metabolism of phenol and hexadecane; better removal of hexadecane was achieved when the suspension was prepared with oxygen (90%) rather than air (70%). Methods for application of the colloidal air in the field are still in the developmental stages. In addition, biodegradation of the surfactants used in the preparation of the colloidal gas aphrons has also not been addressed.

3. Advantages and Disadvantages of Aerobic In Situ Biostimulation Processes

There are a number of advantages and disadvantages in using in situ biorestoration (Table 2). Compounds ranging from petroleum hydrocarbons to solvents have been treated by in situ biorestoration (Table 3). Unlike many aquifer remediation techniques, in situ bioreclamation can often treat contaminants that are sorbed to soil or trapped in pore spaces. In addition to treatment of the saturated zone, organics held in the unsaturated and capillary zone can be treated when an infiltration gallery or soil flushing is used. Biodegradation in the subsurface can be enhanced by increasing the concentration of dissolved oxygen through the use of hydrogen peroxide. ozone, or a colloidal dispersion of air (colloidal gas aphrons). Complete biodegradation (mineralization) of organic compounds usually produces carbon dioxide, water, and an increase in cell mass. However, incomplete degradation (biotransformation) of organic materials can produce byproducts that are more toxic than the parent molecule. An example of biotransformation is the degradation of isopropanol to acetone at a hazardous waste site described by Flathman and Githens.74 The levels of acetone increased initially, but declined after most of the isopropanol was removed. In situ biorestoration may rely on the biodegradation potential of the indigenous subsurface microflora which usually contains few pathogenic organisms unless the aquifer has been contaminated with waste-

Table 2

ADVANTAGES AND DISADVANTAGES OF BIORESTORATION 113.114

Advantages

Can be used to treat hydrocarbons and certain organic compounds, especially water-soluble pollutants and low levels of other compounds that would be difficult to remove by other methods Environmentally sound because it does not usually generate waste products and typically results in complete degradation of the contaminants Utilizes the indigenous microflora and does not introduce potentially harmful organisms Fast, safe, and generally economical Treatment moves with the ground water Good for short-term treatment of organic contaminated ground water Disadvantages Can be inhibited by heavy metals and some organics Bacteria can plug the soil and reduce circulation Introduction of nutrients could adversely affect nearby surface waters Residues may cause taste and odor problems Labor and maintenance requirements may be high, especially for long-term treatment Long-term effects are unknown May not work for aquifers with low permeabilities that do not permit adequate circulation of nutrients

waters.² The time required to treat subsurface pollution using *in situ* biorestoration can often be faster than withdrawal and treatment procedures. A gasoline spill in Ambler, Penn., was remediated in 18 months using *in situ* biorestoration, whereas pump and treat techniques were estimated to require 100 years to reduce the concentrations of gasoline to potable levels.⁶² In situ biorestoration can also cost less than other remedial options. Flathman and Githens⁷⁴ estimated that the cost of *in situ* biorestoration would be one fifth of that for excavation and disposal of soil contaminated with isopropanol and tetrahydrofuran and in addition would provide an ultimate disposal solution. The areal zone of treatment using biorestoration can be larger than other remedial technologies because the treatment moves with the plume and can reach areas which would otherwise be inaccessible.

There are also disadvantages to in situ biorestoration programs. Many organic compounds in the subsurface are resistant to degradation. In situ biorestoration requires an acclimated population; however, adapted populations may not develop for recent spills or recalcitrant compounds. Heavy metals and toxic concentrations of organics may inhibit microbial activity and preclude the use of the indigenous microflora for in situ biorestoration at some sites. One option in this instance would be to remove the inhibitory substances and then seed the subsurface with appropriately adapted microorganisms; however, the benefits to adding microorganisms to the subsurface are still undemonstrated. The formation and injection wells may clog from profuse microbial growth which results from the addition of oxygen and nutrients. In one biostimulation project, microbial growth produced foaming in the well casings.⁶² In addition, the hydrodynamics of the restoration program must be properly managed. The nutrients added must be contained within the treatment zone because the transport of inorganics into untargeted areas can result in eutrophication. High concentrations of nitrate can render ground water unpotable. Metabolites of partial degradation of organic compounds may impart objectionable tastes and odors. For example, the incomplete degradation of gasoline under low dissolved oxygen conditions resulted in phenol production; phenol was then degraded when more aerobic conditions were achieved.⁷² Biostimulation projects require continuous monitoring and maintenance for successful treatment: whether these requirements are greater than those for other remedial actions is debatable. The process results in increased microbial biomass that can exert an oxygen demand that can drive the system anaerobic and result in the production of hydrogen sulfide or other objectionable byproducts. The long-term effects of biorestoration are unknown. In situ biorestoration is difficult to implement in low-permeability aquifers in which perfusion of nutrients and oxygen is slow or negligible; however, many in situ physical and chemical remediation processes

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Table 3 CONTAMINANTS TREATED BY IN SITU BIOSTIMULATION

Contaminants	Treatment description	Ref.
High octane gasoline	Air sparging with nitrogen and phos- phorus addition	6164
Gasoline	Air sparging with complete mix of inorganics	72
Gasoline	Air sparging with addition of com- plete inorganic nutrient solution	78
Gasoline	Air sparging and addition of nutrients	81
Gasoline	Dissolved oxygen supplied by an air stripper and sparging: nutrients also added	86, 99
Gasoline	Dissolved oxygen supplied by an air stripper	87
Gasoline	Hydrogen peroxide plus nutrients	69
Gasoline	Initial treatment utilized air stripping; hydrogen peroxide used later with the nutrient formulation	87, 98, 99
Unleaded gasoline	Hydrogen peroxide supplied the oxygen	101
Mineral oil hydrocarbons	Withdrawn water treated with ozone and reinfiltrated	108
Gasoline	Soil venting used to supply oxygen to unsaturated zone	71
Waste solvents and alkanes	Nutrients plus hydrogen peroxide	79, 87, 96, 100
Methyl chloride, n-bu- tanol, dimethyl aniline, acetone	Withdrawal and treatment by an acti- vated sludge process and recharge of aerated nutrient-laden water	27, 80
Methylene chloride	Withdrawal and treatment with air stripping followed later by treatment in an activated sludge unit and recharge	75, 88
Ethylene glycol	Treatment following withdrawal with ethylene-degrading bacteria and nu- trients and then recharge	75, 89
Isopropanoi and tetrahydrofuran	Treatment in an above-ground reactor with addition of acclimated microbes to the aquifer along with nutrients	74
Aliphatic hydrocarbon plasticizer	Activated sludge and recharge of ac- climated bacteria and nutrients	90
Chloroform	Activated sludge bioreactor with the bacteria innoculated into the subsurface	90

are subject to the same restrictions. The success of *in situ* treatment schemes in lowpermeability aquifers depends on transporting the nutrients to the microflora or the active agent to the contaminants. The process has been used in a variety of hydrogeological formations (Table 4).

4. Related and Innovative Processes

There are a number of innovative, generally unproven, processes that potentially can be applied to *in situ* biorestoration. These processes include land treatment, techniques that decrease the surface tension to enhance the mobility and improve the biodegradability of the contaminants, application of enzymes, and treatment beds.

a. Land Treatment

Land treatment is a process in which the indigenous microflora in surface soils degrade

Table 4TYPES OF AQUIFERS WHERE IN SITU BIOSTIMULATIONHAS BEEN UTILIZED

Aquifer description	Flow characteristics	Ref.	
High permeability dolomite	Pumping rate of 265-378 {/min	6164	
Medium to coarse sand	Pumping rate of 65-151 Umin	9 7	
Alluvial fan deposit of sand, gravel, and cobbles with some clay and silt	Flow of 2.4 m/day	78	
Poorly sorted mixture of boulders, pebbles, cobbles, sand, silt, and clay	Hydraulic conductivity of 9.4 \times 10 ⁻³ -1.7 \times 10 ⁻³ cm/sec	27, 80	
Perched water table in un- stratified, unsorted layer of clay, silts, sands, gravels, and cobbles above a clay layer	Pumping rate of 38—57 (/min	75, 88	
Tank vault filled with pea gravel surrounded by sand and sandy clay strata	Flow rate in excess 100 m/yr; pumping rate of 151 (/min	79, 87, 100	
Glacial outwash composed of silt, sand, and gravel	Hydraulic conductivity of 8.8 \times 10^{-4} —1.5 \times 10^{-3} cm/sec	101	
Coarse sands and gravel	Hydraulic conductivity of 2.1 cm/ sec	108	
Shale and siltstone	Pumping rate of 68 l/min	87, 98, 99	
Coarse sand with greater than 5% gravel	Gradient of 0.015-0.02 m/m; flow of 0.61-0.91 m/yr	69	
Glacial till composed of sand, gravel, and boulders in a silty clay matrix con- nected to a fractured sandstone	•	99	
Shallow basin containing sand and pea grave?	Flow of 27 to 38 ℓ/min	74	

Table 5

FACTORS THAT CONTROL BIODEGRADATION IN LAND TREATMENT¹¹⁷

Chemical structure of the waste Presence of appropriate numbers of microorganisms capable of degrading the wastes Concentration of the wastes Supply of oxygen Optimal water content of between 25 and 85% of the water-holding capacity Optimal temperatures between 20 and 30°C Optimal pH levels between 6 and 8 Availability of inorganic nutrients, principally nitrogen and phosphorus

the organic material contained in the soil. Loehr and Malina¹¹⁵ suggested that land treatment is useful for disposal of organic wastes from municipal sludge, petroleum, wood preserving, leather tanning, coal gasification/liquefaction, food processing, and pulp and paper production. Land treatment involves the addition of the organic waste to the soil, mixing to aerate and incorporate the organics into the soil, and, if needed, adding fertilizer to stimulate microbial activity. The process must be carefully managed to prevent overloading the assimilative capacity of the soil and to prevent migration of the inorganic nutrients, organics, and heavy metals.¹¹⁶ Major factors that control biodegradation in land treatment are listed in Table 5. Land treatment may be advantageous in comparison to other remedial techniques because it requires minimal operation and maintenance and is a proven technology for some

50

wastes.¹¹⁸ However, the process may result in incomplete destruction of the organic wastes. the soil may be difficult to aerate effectively, the wastes must be contained within the treatment zone, air pollution may result, and large areas of land are required. Land treatment is usually limited to the upper 1.5 m of soil,¹¹⁹ which restricts its use in aquifer remediation. However, land treatment may be used to treat excavated soil or wastes that are concentrated at the water table of shallow aquifers. In a survey of treatment options for ground water contaminated with gasoline, the Law Engineering Testing Company¹²⁰ recommended that land treatment be considered when a suitable site is available. In comparison to other treatment technologies, land treatment was highly rated on the basis of effectiveness, capital costs, reliability, and operability.¹²¹

Land treatment was used to treat a spill of 1.9 million ℓ of kerosene.¹²² About 200 m³ of soil was excavated and the contaminated ground water was withdrawn and treated. The contaminated soil was treated by adding lime and fertilizer (nitrogen, phosphorus, and potassium in the ratio of 10:1:0.85) and frequently tilling the soil to a depth of 46 cm. The fastest rate of kerosene degradation occurred during the warmer months of July and August. The concentration of kerosene was reduced from 0.87% to innocuous levels in the upper 30 cm of soil during a 21-month period. However, kerosene persisted at a depth of 30 to 45 cm, perhaps a result of reduced aeration. Within the first 7 months, most of the n-alkanes and unresolved hydrocarbons were degraded. A test for phytotoxicity after land treatment indicated that the phytotoxicity of the kerosene had been reduced but not completely eliminated; crop yields were 20% below those in a control area 23 months after the spill.

b. Techniques That Reduce the Interfacial Tension

Insoluble organic compounds that are sorbed to soils can be mobilized and made more available for microbial attack by decreasing the interfacial tension between the compounds and water. The interfacial tension can be decreased with dispersants, surfactants, extractants, and emulsifiers. Dispersants have been used in remediation programs to control marine oil spills with some success.¹²³ Addition of dispersants can increase the rate of reaction, but may not increase the extent of hydrocarbon degradation. However, not all dispersants enhance degradation of hydrocarbons and some may be toxic to microorganisms. Mulkins-Phillips and Stewart¹²⁴ reported that only one of four dispersants stimulated biodegradation of crude oil by marine bacteria; however, all four dispersants caused shifts in the microbial population.

The addition of surfactants to mobilize organics sorbed to soils has been tested in laboratory studies. A combination of nonionic and ionic surfactants was most effective in removing gasoline from sand columns by simple displacement and by draining the gasoline from the capillary zone.¹²⁵ Some of the surfactants identified in this study were biodegradable, whereas others exhibited varying degrees of toxicity. Ellis et al.¹²⁶ demonstrated that surfactants could remove up to 95% of the crude oil and polychlorinated biphenyls trapped in sand columns, whereas aqueous washes failed to remove appreciable quantities of these contaminants. Surfactants may be used in combination with biorestoration to remediate aquifer contamination problems. A surfactant wash can mobilize the residual hydrocarbon in the unsaturated zone and render trapped hydrocarbon in the saturated zones more available for biodegradation.⁹² A surfactant which is biodegradable and nontoxic is required. The application of surfactants to subsurface contaminants may present additional environmental problems by spreading contaminants to sections of the aquifer previously uncontaminated.

Emulsifers can be used to increase the surface area and render the oil more degradable.¹²⁷ Emulsifiers can be either chemical additives or biological agents. Robichaux and Myrick¹²⁸ reported that one chemical emulsifier increased the microbial decomposition of oil 18-fold; however, other emulsifiers were less successful and many may have been toxic. Broderick and Cooney¹²⁹ reported that emulsifiers are produced by a variety of organisms in freshwater environments, especially those associated with sediments. Laboratory studies conducted by Vanlooke et al.¹³⁰ showed that 10 to 20% of the oil adsorbed to soil was removed after the

addition of a nutrient solution containing ammonium nitrate and peptone: microbial metabolites were thought to be responsible for the enhanced desorption. The ground water microflora in an aquifer contaminated with aviation fuel was reported to emulsify hydrocarbon when supplied with dissolved oxygen, nitrogen, and phosphorus.¹³¹ Micelles and microemulsions of the hydrocarbon are likely to be formed by bioemulsifiers which may facilitate transport of the hydrocarbon into the cell.¹³² Biosurfactant-producing bacteria may be used to remediate contaminated aquifers but their use will be controlled by: (1) the physical and chemical characteristics of the contaminant: (2) the geophysical and geochemical characteristics of the formation such as pore size distribution and permeability, water quality, and oxygen concentration; and (3) competition with indigenous microflora. The hydrocarbon that is mobilized as a result of bioemulsification may be withdrawn from the aquifer and treated by above-ground techniques.¹³³ The microbial conversion of the hydrocarbons to more polar compounds such as alcohols, ketones, phenols, or organic acids will also mobilize the contaminants.

Another application of bioemulsifiers is enhanced oil recovery. Clark et al.¹¹⁴ found several aerobic microbial species that could be used to bioemulsify oil *in situ*. Zajic and Akit¹³⁵ found two bacterial strains that produced high concentrations of surfactants; one could remove bitumen from tar sands when grown on hexadecane. A bacterial culture supported on molasses was able to release 19.5 to 48.7% and utilize 2 to 51% of the oil in a formation within 10 days.¹³⁶ Field trials were successful in two of seven reservoirs, increasing yields by 10 to 200%.

Extraction techniques such as steam flooding, alcohol flooding, and thermal flooding also may be used to mobilize organic contaminants in the subsurface; however, they have not been demonstrated in the field.¹³⁷ Horizontal or vertical water sweeps can be used in permeable aquifers to reduce the quantity of hydrocarbons before treatment by other methods such as *in situ* biorestoration.

c. Enzymes as an Innovative Treatment Technique

Another innovative *in situ* process is the addition of enzymes to degrade specific organic compounds. In one investigation, a parathion hydrolase enyzme isolated from a mixed culture of *Pseudomonas* was added to wet and dry plots of soil amended with the organic phosphorus insecticide diazinon.¹³⁸ In both wet and dry plots, removal was initially faster in the enzyme-amended soil than in the control; however, diazinon levels in the test and control plots were similar after 408 hr. The effectiveness of an enzyme depends upon its stability in the environment and contact with the substrate. Adequate mixing to insure contact may be difficult to achieve in an aquifer. In addition, enzymes may be better substrates for microbial metabolism than many organic pollutants. The stability of an enzyme in the environment may be adversely affected by changes in pH and solute concentrations.

d. Treatment Beds

Treatment beds are another innovative process currently under development. The process consists of a trench which intercepts contaminated ground water and either a biological or chemical treatment bed which removes the contaminants. Chemical treatment beds for organic compounds include activated carbon or synthetic resins.¹³⁹ Biological treatment can be accomplished using processes similar to trickling filters in which microorganisms colonizing a surface are supplied with oxygen and nutrients. if necessary, and degrade the contaminants which enter the treatment bed. Permeable treatment beds may plug or exhibit channeling, which reduces their effectiveness. Similar results could be obtained without the treatment bed by implementing *in situ* biorestoration in a narrow zone that intercepts and contains the plume.

- 5. Potential for Anaerobic Processes
- a. Anaerobic Degradation Pathways in the Subsurface

Anaerobic processes are important in the subsurface environment because oxygen may

be depleted in contaminated aquifers as a result of aerobic microbial activity. However, lowlevels of oxygen will support some microbial activity. Once the dissolved oxygen content in ground water declines as a result of microbial activity, replacement depends on recharge, reaeration from soil gases, and mixture with oxygenated waters surrounding the organic plume.^{140,141}

Degradation of a variety of compounds under anaerobic conditions has been demonstrated to occur in aquifers and laboratory experiments using subsurface materials. However, anaerobiosis may retard the degradation of many compounds.⁴⁷ The sequence of microbial processes that occur as environmental conditions change from aerobic to anaerobic in the subsurface usually follows the pattern of aerobic respiration, denitrification, manganese and iron reduction, sulfate reduction, and finally methane formation.^{142,143} Net energy production decreases as the redox potential decreases.¹⁴⁵ Bouwer and McCarty^{42,144} demonstrated differences in the degradation of organic compounds under different redox potentials: chloroform and 1.1.1-trichloroethane were degraded by methanogenic, but not denitrifying, bacteria. Ehrlich et al.^{21,145} reported the degradation of phenolics, but not polynuclear aromatics such as naphthalene, under methanogenic conditions. Recently Kuhn et al.²⁹ documented removal of tetrachloroethylene, the xylene isomers, and dichlorobenzene isomers under denitrifying conditions. Wilson and Rees³⁸ showed that degradation of benzene, ethylbenzene, toluene, and o-xylene occurred in methanogenic aquifer material from a landfill. although the process was slow compared with aerobic pathways. The concentration of toluene had been reduced by 87% after 6 weeks, however, more than 20% of the benzene, ethvlbenzene, and o-xylene added to the microcosms persisted beyond 40 weeks. In the same study, trichloroethylene and styrene degraded under anaerobic conditions, whereas chlorobenzene persisted. Suflita and Gibson⁴³ reported that 13 of 19 halogenated isomers of benzoate, phenol, and phenoxyacetate persisted at concentrations >90% of that initially added to subsurface materials collected from a sulfate-reducing zone; however, only 3.4dichlorobenzene remained at concentrations >5% of that originally added to methanogenic samples collected downgradient of the sulfate-reducing zone. Maximal numbers of sulfatereducing and methanogenic bacteria are found at redox potentials of -100 to -150 and -250 to -350 mV, respectively.¹⁴⁶ Halogenated aliphatics such as trichloroethylene, tetrachloroethylene, carbon tetrachloride, and 1,1,1-trichloroethane can be mineralized or dehalogenated under reducing conditions¹⁴⁷ to potentially more toxic compounds such as vinyl chloride. 148, 149 Tiedje et al. 150 reported the anaerobic degradation of many other compounds by organisms from a variety of environments.

b. Anaerobic Processes in In Situ Biostimulation

Anaerobic processes may be of potential use in *in situ* biorestoration processes. The redox potential could be selectively adjusted to favor the degradation of a particular contaminant. In addition to adjusting the redox potential, the pH of the ground water could be adjusted to the neutral or alkaline conditions required for sulfate reduction, methanogenesis, and usually denitrification. Anaerobic degradation of organic compounds would probably require less inorganic nutrient supplementation because less energy, and therefore biomass, is produced.¹¹³ Batterman¹⁵¹ added nitrate to ground water contaminated with hydrocarbons in an attempt to promote denitrification. The contaminated aquifer consisted of an 8- to 10-m thick layer of sand which contained some silt and clay beds and a ground water flow of 4 m/day. The water was withdrawn from a deeper uncontaminated aquifer, aerated, passed through a sand filter, and amended with nitrate at 300 mg/ ℓ before being recharged to the shallow aquifer. Phosphate was not added because it was not limiting. The authors suggested that anaerobic degradation accounted for the removal of 7.5 tons of hydrocarbon within a period of 120 days. Removal of 1 mg of the hydrocarbon required 3.3 mg of nitrate. 152 The concentration of aliphatics declined slowly from 1.5 to about 0.7 mg/ ℓ , whereas the concentration of total aromatics declined from 5.5 mg/ ℓ down to about 1.5 mg/ ℓ in approximately

1 year. The rate of decline in the concentration of xylene was much slower than that of benzene and toluene. Water was injected during the test, which resulted in a rise in the level of the hydrocarbons as well as the water table into the unsaturated zone. There was an overall 40% reduction in the concentration of hydrocarbon as a result of the treatment process. Insufficient information was provided to determine if anaerobic degradation was responsible for the removal of the contaminants or if the removal was due to the oxygen introduced when the injection water was aerated before it was recharged into the shallow aquifer.

Degradation of low concentrations of organic compounds under methanogenic conditions, with acetate added at higher concentrations as a primary substrate, has been demonstrated.¹⁴² McCarty¹⁵³ proposed a scheme to treat contaminated ground water anaerobically using the primary substrate concept. The system consists of an above-ground reactor to which substrate and nutrients are added, a well casing bioreactor which operates anaerobically like a trickling filter, and the aquifer. The above-ground reactor is used to develop an acclimated population. The effluent from the above-ground reactor is injected into the well casing bioreactor to introduce acclimated microbes into the aquifer or enhance adaptation of the indigenous population to the contaminants. Once the acclimated population has developed, use of the above-ground reactor can be discontinued.

A method that utilizes sequential aerobic and anaerobic conditions to degrade hazardous wastes has been studied in soils and may be applicable to subsurface cleanup. An insecticide, methoxychlor, was slightly degraded in soil under either aerobic or anaerobic conditions after 3 months of incubation. When the samples were converted from an anaerobic to an aerobic status, mineralization of the methoxychlor increased 10 to 70 times of that observed in soils maintained aerobically throughout the incubation period.¹⁵⁴ The enhancement in methoxychlor degradation in soils exposed to anaerobic conditions and degradation of the dechlorinated products under aerobic conditions. This anaerobic-aerobic treatment scheme may be useful in biorestoration of aquifers contaminated with halogenated compounds. The aquifer could be managed like a sequencing batch reactor in which an acclimated population is exposed to deoxygenated water, then to aerobic conditions, and then the treated water is withdrawn. The hydraulically managed system is then allowed to sit idle until the next cycle is initiated.

Rates of degradation under anaerobic conditions are typically slower than those under aerobic conditions; in addition, organic compounds may not be mineralized under anaerobic conditions even after long periods of incubation.³⁸ However, anaerobic treatment may be required to degrade pollutants that are reclacitrant under aerobic conditions; also, anaerobic treatment may require less management. The application of anaerobic conditions to biorestoration is still in the developmental stage and more research is required to demonstrate its usefulness in the field.

C. Addition of Specialized Microbial Populations to the Subsurface

In addition to stimulating the indigenous microbial population to degrade organic compounds, another innovative but not yet fully demonstrated technique is to add microorganisms with specific metabolic capabilities to the subsurface.⁴ Specialized organisms may be inoculated into the subsurface environment or the environment may be altered to favor growth of a population with specific metabolic capacities. Populations that are specialized in degrading target compounds are selected by enrichment culturing or genetic manipulation. Enrichment culturing involves exposure of microorganisms to increasing concentrations of a contaminant or mixture of contaminants. The type of microorganism that is selected, or in essence acclimates to the contaminant, depends on the source of the inoculum, the conditions used for the enrichment, and the substrate.¹²⁷ Acclimation can result from an increase in the number of organisms that can degrade the contaminant, new metabolic capabilities that result from genetic changes, or an increase in the quantity of the enzymes necessary for the transformation.¹⁵⁵ The genetic changes include overproduction of enzymes, inactivation or alteration of regulatory gene control, or production of enzymes with altered specificities.¹⁵⁶

Genetic manipulation of microorganisms to produce specialized populations that can degrade target contaminants is a relatively recent development. According to Kilbane,¹⁵⁷ genetic engineering may accelerate and focus the process of evolution. Genetic manipulation can be accomplished by two different methods. In the first method, the organisms are exposed to a mutagen such as UV light, nitrous oxide, or 8-azaquinonone, and then a population with specialized degradative capabilities is isolated by enrichment culturing;^{158,159} however. this may produce weakened strains because the process is nonspecific and affects the entire genome.¹⁶⁰ In the second method, recombinant DNA technology is used to change the genetic structure of the microorganism.¹⁵⁷ The genetic structure is changed by inserting a DNA fragment, often a plasmid that codes for a specific degradative pathway, into another organism. A plasmid is a piece of DNA that exists independently from the chromosomes of the cell.¹⁶⁰ The extra-chromosomal DNA can be transformed from one bacterium to another by conjugation, transduction, or transformation. Multiple degradative capabilities can be placed on a single plasmid that will allow the organism to degrade an array of compounds or complete the degradation of a recalcitrant molecule. Genetic engineering can be used to stabilize the degradative traits coded by the plasmid, increase the number of plasmids in a cell, amplify enzyme production and activity, invoke multiple degradative traits, or produce a novel degradative pathway.¹⁶¹ In addition, organisms with different substrate affinities, pH optima, or degradation rates can be fashioned.¹⁶²

1. Genetic Engineering to Enhance Degradative Activity

Genetic engineering has been used to enhance the degradation of the recalcitrant pesticide, 2,4,5-trichlorophenoxyacetic acid (2,4,5-T). Biodegradation of the pesticide is usually very slow.¹⁶³ A mixed culture of microorganisms that uses 2.4.5-T as the sole carbon and energy source was obtained by a technique called plasmid-assisted molecular breeding.¹⁰⁴ The technique involves inoculating a chemostat with microorganisms from a variety of hazardous waste sites and organisms that carry an array of plasmids that code for degradation of specific xenobiotics. A pure culture that could use 2,4,5-T as the sole carbon and energy source was isolated from the mixed population and tentatively identified as *Pseudomonas cepacia*.¹⁶⁵ In addition, the culture, designated P. cepacia AC1100, was reported to oxidize many chlorophenols. Degradation of both 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4.5-T was expressed in another strain of P. cepacia after conjugal transfer of two plasmids from an Alcaligenes entrophs sp. that degraded some chlorinated phenoxy herbicides.¹⁵⁰ An inoculum of 2 \times 10⁷ cells/g of P. cepacia AC1100 degraded 95% of the 1000 mg/ ℓ 2.4.5-T added to soil at 25% moisture and incubated at 30°C.¹⁶⁶ Less 2,4,5-T was removed with a smaller inoculum size and different temperatures and moisture contents. In addition, the 2.4.5-Tdegrading bacteria did not survive in soil without 2,4.5-T or when the concentration of the compound had been depleted.¹⁶⁵ Field trials to determine the effectiveness of the 2.4.5-Tdegrading bacteria have not been conducted.

Colaruotolo et al.¹⁶⁷ received a patent for "microbial degradation of obnoxious organic wastes into innocuous materials." The process involves isolation of microbial cultures from samples of soil and leachate from a hazardous waste site by enrichment culturing and then application of the purified strains in the field to remove the contaminants. Microorganisms capable of degrading selected isomers of chlorotoluene, dichlorotoluene, and dichlorobenzoate were isolated. Conjugation and transformation experiments were conducted to transfer the plasmid DNA, which conferred the ability to degrade some chloroaromatics, from the original isolates to another organism. The patent claimed that the organisms could be used to decontaminate soil, remove contaminants in the air, mineralize toxic organics in the leachate from a chemical landfill, and thereby reduce the concentrations of noxious chemicals.

Table 6 REASONS WHY INTRODUCED ORGANISMS FAIL TO FUNCTION IN THE ENVIRONMENT¹⁷¹

The concentration of the compound is too low

The environment contains some substance or organisms that inhibit growth or activity, including predators. The inoculated organism uses some other organic other than the one it was selected to metabolize. The organic is not accessible to the organism.

2. Issues in Genetic Engineering of Microbes

Organisms that cannot easily exchange their genetic information with other organisms and are restricted to growth under defined environmental conditions are preferred candidates for genetic manipulation.¹⁶¹ Issues concerning the use of genetically engineered organisms in the environment include (1) adverse effects on human health. (2) how to effectively monitor their dispersal. (3) survival of the engineered organism in the environment. (4) regulation of activity in nontarget areas; and (5) determination of set risk levels acceptable to the public, 108 Many scientists argue that the engineered organism is not radically different from that which is genetically unaltered. The release of genetically engineered organisms into the environment is of great concern to some and some time may elapse before these organisms are used.¹⁶⁹ The survivability of genetically altered organisms in the environment is also of concern. Surrogates of genetically engineered organisms which carried antibiotic resistance were added to samples of sewage, lake water, and soil and survived at rates that varied with the strain and environment tested.¹⁷⁰ Some of the antibiotic-resistant strains reached steadystate concentrations in lake water and sewage; however, all strains declined in the soil after a period of 1 month. Pseudomonas strains that degrade 2,4-dichlorophenol and p-nitrophenol were isolated from soil by enrichment-culturing techniques.¹⁷¹ The ability of the isolates to degrade the phenol derivatives was variable when inoculated into lake water, sewage, and soil.

Inoculation of a specialized microbial population into the environment may not produce the desired results for many reasons (Table 6).¹⁷¹ The concentration of the target compound required to support activity of a specific degrader may be limiting. Toxic or antimicrobial substances such as antibiotics may be found in many environments. High-density inocula may be grazed by predators and the degradative capacity severely decreased if the growth rate of the introduced organisms is slow. In addition, adequate mixing to ensure contact of the organism with the pollutant will be difficult to achieve in the subsurface.

Most hazardous waste sites involve contamination of the environment with more than one compound. Therefore a mixture of organisms may be necessary to degrade all of the compounds in the waste.¹²⁷ Populations that have adapted to degrade many organic contaminants may be isolated from biological treatment processes, such as sewage treatment, which recieve pollutants. The efficacy of an inoculated population of specific degraders will depend on environmental constraints such as temperature, pH, and the concentrations of substrate, nutrients, and oxygen. 127,172 Successful results from inoculation of foreign organisms are more likely in simple environments because the environment can be controlled more easily. An example of inoculation into a simple environment would be the introduction of bacteria into a biological reactor, oil tanker ballast tanks, or fermentator; these also provide the benefit of containing the microorganisms. To avoid problems encountered with inoculation of foreign organisms into the environment, samples from the contaminated environment can be collected, microorganisms that can degrade the pollutants can be cultured by enrichment techniques or genetically engineered, and finally the specialized population can be reintroduced into the environment from which they came.¹⁷³ In addition, genetic manipulation of oligotrophic bacteria with high-affinity enzyme systems may be advantageous because these enzyme systems will allow the organism to attack low concentrations of organic pollutants.¹⁷⁴

3. Seeding Aqueous Environments with Microorganisms

Inoculants of specialized microorganisms have been used in treatment of contaminated water. Atlas and Bartha¹⁷⁵ tested several commercial bacterial preparations and found that the inocula were ineffective in treating oil spills in the marine environment. However, the addition of fertilizer and a bacterial seed isolated from an estuarine environment increased petroleum degradation in a saline but not in a freshwater pond.¹⁷⁶ After 6 weeks, 50% of the oil remained in the saline pond. The lack of activity in the freshwater pond suggests that the inoculum should be cultured from an environment similar to that being treated. Colwell and Walker¹²³ suggested that seeding would be unsuccessful in environments such as the ocean; however, contained spills and lagoons may be amenable to such treatment. Gutnick and Rosenberg¹⁷⁷ stated that "there is no evidence to support the claim that 'seeding' oil slicks with microorganisms reduces oil pollution by stimulating petroleum biodegradation."

4. Seeding Soil Environments with Microorganisms

The efficacy of inoculating soil with acclimated bacteria to remove selected contaminants was tested in a series of experiments¹⁷⁸ using experimental chambers set up in greenhouses. The contaminants, aniline and formaldehyde, were added to three types of soils (clay, sandy loam, and organic-rich) and plants were seeded in the chambers. Removal of the contaminants by a mixed microbial population from primary sewage effluent and an acclimated population was investigated. Formaldehyde was not removed in organic soils amended with sewage and acclimated bacteria: however, this treatment was successful in the upper and middle zones of the sand and clay soils. Aniline was removed in the organic and sandy soils after a second application of sewage microorganisms, nutrients, and yeast extract. Chemical oxidation of the organics using hydrogen peroxide was effective in reducing aniline concentrations. None of the treatments were successful in removing aniline from the clay soil. The removal of chlordane and 2,4-dinitrophenol by mutant-adapted microbial cultures was also investigated. The inoculum was successful in degrading 2,4-dinitrophenol from the upper layer of the clay soil only. The authors suggested that the sewage inoculum was a low-cost, effective method for removal of aniline and formaldehyde in most soil types: however, addition of the adapted population was not successful in these tests.

Inoculation of soils to remove chlorinated organics and pesticides has been attempted. Daughton and Hsieh¹⁷⁹ reported that inoculation of sterilized soils with a parathion-acclimated culture reduced the concentration of the insecticide by 85%; however, the efficiency of the inoculum in nonsterile soil was greatly reduced. Focht and Brunner¹⁸⁰ used an *Acinetobacter* strain as an inoculum to degrade biphenyl and polychlorinated biphenyls (PCBs) in soils. The inoculum increased the initial and maximum mineralization rates and the disappearance of the more heavily chlorinated biphenyls, but the overall extent of mineralization of PCBs was not greater than that in uninoculated soil to which biphenyl had been added. The process was thought to be a cometabolic-commensal metabolism of the PCBs.

Remediation of soil contaminated with hydrocarbons by inoculating with hydrocarbondegrading organisms has been met with varying success. Schwendinger¹⁸¹ demonstrated that inoculation of a hydrocarbon-degrading strain of *Cellumonas* in soil contaminated with petroleum increased the rate of reclamation in comparison to soils amended with only nutrients. Jobson et al.¹⁸² reported that the application of 10° cells of oil-degrading bacteria per cubic centimeter of soil slightly increased the degradation of the C_{20} - to C_{28} -group of n-alkanes in comparison to soils amended with fertilizer only. However, Lehtomaki and Niemela¹⁸³ reported that Brewer's yeast added to soils served primarily as a fertilizer rather than as an inoculum to actively degrade the oil. Seeding boreal soil with an oil-degrading inoculum increased microbial activity.¹⁸⁴ In laboratory studies, the addition of 300 ppm nitrogen and 100 ppm phosphorus, inoculation, and adjusting the pH to 7 increased microbial activity by at least a factor of four in comparison to unamended samples after 40 days of incubation. An increase in plant growth in an oil-contaminated area in response to fertilizer

addition was shown in field studies; however, the increased growth could have resulted from the addition of fertilizer or enhanced removal of the petroleum. In contrast, Westlake et al.¹⁸⁵ reported no beneficial effects from the addition of oil-degrading bacteria to boreal soils. The lack of enhancement may be a result of inadequate application of the inoculum. The type of organisms isolated from enrichment culturing depends on conditions used during the isolation procedure. For example, enrichments made at 4 and 20°C contained different organisms, and cultures enriched on a low-quality crude were better adapted to utilize a lower quality crude than cultures enriched on a high-quality crude.¹⁸⁶ These data suggest that enrichments for specialized populations should be conducted using the environmental conditions and contaminants that are unique to the site under investigation.

An inoculum of pentachlorophenol-degrading organisms has been used to decontaminate soil, river water, ground water, and other freshwaters.¹⁸⁷ A *Flavobacterium* sp. that could mineralize pentachlorophenol (PCP) was isolated from a man-made channel which was exposed to the compound for several weeks.¹⁸⁸ In addition to mineralizing PCP, the microorganism could attack a number of other chlorinated phenols but not all isomers.¹⁸⁹ The *Flavobacterium* sp. at a cell density of 10⁶ cells/mℓ removed over 90% of the PCP added to river water, ground water, and other fresh waters, usually within 48 hr.¹⁸⁷ The organisms' ability to degrade PCP was best between 15 and 35°C and at pH values between 7.5 and 9. Inoculum densities as low as 10⁴ cells/mℓ resulted in efficient removal of PCP. The time required to remove the PCP increased with increasing concentrations of PCP. When added to uncontaminated soil, the PCP was rapidly mineralized.¹⁸⁸ The highest extent of mineralization occurred in soils with moisture contents between 15 to 20%.

Mineralization of PCP was observed at inoculum densities as low as 3.1×10^3 cells/g: however, a slightly higher extent of mineralization was observed at a cell density of $3.1 \times$ 10° cells/g.¹⁸⁸ Mineralization of PCP in one uninoculated soil began after 7 days of incubation and mineralization proceeded to the same point as the sample inoculated with 10⁷ cells/g. Concentrations of PCP in soil contaminated from a wood-treating landfill were reduced from 298 to 58 ppm after four applications of the inoculum in a period of 100 days. In another contaminated soil, PCP levels were reduced from 321 to 41 ppm after one application of seed, but similar levels of removal were observed in the uninoculated control. The seed could not remove PCP from a third soil in which the concentration of PCP had been diluted tenfold to 553 ppm and the pH adjusted to neutrality. Addition of 10° cells/g soil of a culture of PCP-degrading Arthrobacter sp. reduced the half-life of PCP from 2 weeks to 15 hr.140 Edgehill and Finn¹⁹¹ reported that the rate of PCP disappearance was proportional to inoculum size that ranged from 10⁴ to 10⁶ cells/g soil. Up to 85% of the PCP was removed within 12 days in soil in which the seed had been thoroughly mixed; however, only 50% was removed in the unmixed soil. Brown et al.¹⁹² suggested that fixed film reactors with a PCP-adapted population may be used to treat waters contaminated with PCP at concentrations below the threshold of toxicity. A consortium that was attached to rocks from an artificial stream amended with PCP was generally able to degrade PCP as fast as the Flavobacterium sp. described by Crawford and Mohn.¹⁸⁸ A treatment system using two fixed film reactors in series was then proposed; the first reactor would reduce high concentrations of PCP and the second reactor would contain organisms that could remove PCP to low levels. The consortium was able to remove PCP to <1 $\mu g/\ell$ when the initial concentrations were <1 g/ℓ .

5. Seeding the Subsurface with Microorganisms

Inoculation of bacteria into the subsurface for biorestoration has been met with some success, but the contribution of the introduced bacteria to the overall cleanup cannot be readily determined. In most cases, the role of the introduced bacteria in degradation of the contaminants cannot be determined because appropriate control plots were not incorporated into the experimental design and the results were not quantitatively measured throughout the course of the project. The biggest concern of inoculation into the subsurface is ensuring

Table 7SUMMARY OF AQUIFER REMEDIATION CASEHISTORIES UTILIZING INTRODUCED ORGANISMS

Compound	Treatment description	Ref.
Acrylonitrile	Mutant bacteria added after con- centrations had been reduced by air-stripping	199
Phenol and chlorophenol	Initial treatment by adsorption onto GAC followed by inoculation with mutant bacteria	199
Ethylene glycol and propyl acetate	Treatment above ground and later with specialized bacteria	200, 201
Dichlorobenzene, dichloromethane, and trichloroethane	Initial treatment with air stripping and then inoculation with a hy- drocarbon-degrading bacteria	200, 201
Unidentified organic compounds	Hydrocarbon-degrading bacteria added after levels reduced by GAC and air stripping	202
Formaldehyde	Commercial degrader added to above-ground treatment system formed from rail ballast	203

contact between the specialized cells and the target contaminants. The cells may be filtered out of the perfusing solution or sorbed onto soil before reaching the contaminants.⁽⁴² In addition, normal die-off may control the movement and spread of bacteria in well-sorted sand, gravels, fractured rock, and karstic limestone.

Microbial movement through the subsurface depends on the characteristics of the soil and microorganisms. Only 1% of an inoculum of a *Pseudomonas* strain passed through a 2-in. sandstone core after washing with 123 pore volumes.¹⁹³ Penetration of bacteria into sandstone cores with hydraulic conductivities >100 mD (hydraulic conductivity = 9.6×10^{-5} cm/sec) was rapid: however, penetration in cores with hydraulic conductivities below 100 mD was slow.¹⁹⁴ Motile bacteria moved three to eight times faster than nonmotile bacteria. Hagedorn¹⁹⁵ summarized the results of selected studies on the maximum distance that microorganisms moved in various soils: 19.8 m in 27 weeks in a fine sand; 10.7 m in a sand and sandy clay in 8 weeks; 24.4 m in a fine and coarse sand (time of travel not reported); 30.5 m in a sand and pea gravel aquifer in 35 hr; 0.6 to 4 m in a fine sandy loam (time of travel not reported); 457.2 m in a coarse gravel aquifer in 15 days; 28.7 m in 24 to 30 hr in a crystalline bedrock. Bacteria have moved as far as 920 m in the subsurface at rates of up to 350 m/day.¹⁹⁶ Microbial movement through soil macropores is an important mechanism of transport in all subsurface soils except sandy soils and those that are disturbed.¹⁹⁷

Transport of microorganisms in the subsurface can occur. However, *in situ* biorestoration programs using inoculation techniques will be affected by adverse conditions that decrease the survival of microorganisms in the environment. Several factors must be considered before an *in situ* biorestoration program utilizing acclimated bacteria is implemented. The source, quantity, nature and biodegradability of the contaminants, and the environmental conditions of the site must be determined.¹⁹⁸ In addition, laboratory tests to determine the kinetics of degradation, the potential for inhibition under various conditions, requirements for oxygen and nutrients, and the effects of temperature should be conducted. The formation must be permeable enough to perfuse nutrients and the inoculum through the zone of contamination.

6. Aquifer Remediation Using Inoculation Techniques

Inoculation of microorganisms into the subsurface has been used in aquifer remediation in conjunction with wastewater treatment processes. These cases are summarized in Table 7. A representative system is shown in Figure 3. In one case study, 26,500 (of acrylonitrile



FIGURE 3. Combination of above-ground treatment with in situ biorestoration.

was spilled in a metropolitan area from a leaking rail car.¹⁹⁹ The receiving aquifer contained significant amounts of silt and clay and hence was rather impermeable. Initial treatment involved withdrawal and treatment of the ground water by air stripping. After the concentration of acrylonitrile had declined to nontoxic levels, mutant bacteria were seeded into the soil. The concentration of acrylonitrile declined from 1000 ppm to nondetectable levels (limit of detection 200 ppb) within 1 month; however, the role of the bacterial seed in acrylonitrile degradation could not be determined.

Quince and Gardner^{200,201} documented the cleanup of 378,500 ℓ of various organic compounds. including ethylene glycol and propyl acetate, over a 23,000-m² area. The soil consisted of a thick silty clay that extended to a depth of more than 15.2 m; migration of the organics into the main aquifer was prevented by the structure of the formation. Containment and recovery of the organics were limited to the perched water table located in the upper clay layer. The contaminated ground water was withdrawn and treated by clarification, aeration, and GAC. A biostimulation program with specialized bacteria, nutrients, and air was initiated after the levels of the contaminants had decreased from 2000 to 10,000 ppm to <200 ppm. During treatment, the concentration of ethylene glycol was reduced from 1200 to <50 mg/ ℓ , propyl acetate was reduced from 500 to <50 mg/ ℓ , and the total concentration of spilled compounds declined from 36,000 to <100 mg/ ℓ . The resulting concentrations of contaminants were acceptable to the regulatory agencies.

Quince and Gardner^{200,201} documented the cleanup of a number of organic chemicals including dichlorobenzene, methylene chloride, and trichloroethane that contaminated the subsurface as a result of a spill from leaking tankers. The treatment scheme included recovery of product with a vacuum system, soil flushing, air stripping, and then inoculation of commercial hydrocarbon-degrading bacteria into an above-ground reactor followed by recharge of the effluent into the subsurface. A commercial microbial inoculum seeded into the above-ground reactor significantly decreased the concentrations of the organic contaminants after 36 hr of exposure. The aeration was terminated after a 95% reduction in the organic levels was achieved. The injected hydrocarbon degraders were expected to complete the biodegradation *in situ*; however, the role of the added bacteria was not demonstrated.

An accidental spill of 492.000 ℓ of organic chemicals entered a 4.6-m thick shallow unconfined aquifer and resulted in total contaminant levels as high as 10.000 ppm.²⁰² A drinking water aquifer was separated from the contaminated zone by 15.2 to 18.3 m of silty clay. The contaminated ground water was withdrawn and treated by clarification. GAC adsorption, and air stripping. A program to enhance *in situ* biological degradation was

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initiated after the concentration of the organics had declined from as high as 10,000 to 1000 ppm. The results of laboratory tests indicated that the indigenous bacteria could degrade the contaminants when supplied with nutrients. Application of a commercial bacterial inoculum did not increase the biodegradation rates of the organics; in fact, one compound (unidentified) was degraded slower by the commercial hydrocarbon-degrading inoculum than the indigenous population. Effluent from the treatment system was amended with hydrocarbon-degrading bacteria, air, and nutrients and injected into the vadose zone. As a result, the concentrations of the contaminants in one soil core were reduced from 800 to 150 mg/ ℓ in 2 months. In another area, the concentration of the chemicals in composited soil samples declined from 24,000 to 2000 mg/ ℓ . The concentrations of the organics in the ground water were reduced to <1 ppm, which met regulatory approval. Incorporation of biological treatment into the restoration program decreased the cost of operation and maintenance. The role of the commercial inoculum in the removal of the contaminants could not be determined; in addition, laboratory studies indicated that the inoculum did not enhance biodegradation.

A spill of 75,700 l of a 50% solution of formaldehyde from a railroad tank car contaminated the soil and railroad bed in Ukiah, Calif.²⁰³ Contaminated surface and ground waters were removed by a vacuum truck and 190 m³ of soil were excavated. Approximately 49 million ℓ of water was collected. The water was initially treated with hydrogen peroxide to reduce the concentration of formaldehyde from 30,000-50,000 to 500-1000 ppm by oxidation. The feasibility of in situ biological degradation of the remaining formaldehyde using a commercial bacterial inoculum was then investigated. A commercial inoculum that contained specially cultured microorganisms was chosen for the project. The biological treatment system consisted of a portable aeration tank, a spray system, and a trickling filter. The ground water was heated to increase the destruction rate and the pH was adjusted as necessary with sulfuric acid or soda ash: nitrogen and phosphorus were added as needed. The inoculum was rehydrated with chlorine-free water and added to the system at a rate of 1.4 kg/day. The concentration of formaldehyde in the treatment tank fell from >700 to about 10 mg/t after 24 days. The oxygen uptake rate in the sump ranged from 12 to 82 mg/t hr⁻¹ and from 29 to 51 mg/ ℓ hr⁻¹ in the ballast gravel. The treatment program was temporarily suspended for 1 day and the system was flushed. During this period, the concentration of formaldehyde increased greatly; however, a rapid reduction in formaldehyde levels to <1 mg/ℓ followed. The authors suggest that the removal of the formaldehyde was a result of biological activity, however, they concede that proving the role of microorganisms in formaldehyde degradation would be difficult. In addition, the role of indigenous and inoculated bacteria in formaldehyde degradation could not be separated.

7. Enrichment of Specific Populations

A strategy often used in industrial microbiology is to search through nature for an organism with specialized metabolic capabilities and then culture that organism in a fermentor to protect it from competition. However, this strategy would be difficult to apply in the subsurface environment because the specialized population must be competitive in addition to performing the desired transformation. Enrichment culturing techniques are often used to isolate organisms with specialized metabolic capabilities. The same concept can be used to identify conditions that favor the colonization of that environment by organisms with special traits.

The microbial utilization of pollutants as carbon and energy sources has already been discussed. This section will emphasize the metabolism of pollutants by microorganisms enriched on other primary substrates.

Oxygenated water-table aquifers are often polluted with chlorinated organic solvents such as trichloroethylene.^{204,205} The ubiquity of these compounds in oxygenated ground water may result from their resistance to microbial attack under aerobic conditions in the subsurface. However, more recent work has indicated that incubation of soils or aquifer materials with

methane, propane, or natural gas will enrich for microorganisms that co-oxidize trichloroethylene and a variety of other halogenated organic compounds.²⁰⁶⁻²¹³ This technique may be applicable to *in situ* restoration of aquifers which are contaminated with chlorinated organic solvents.

Using gaseous aliphatic hydrocarbons as the feedstock for a forced co-oxidation is advantageous because they are nontoxic, relatively inexpensive, and widely available in the form of natural gas, liquified petroleum gas, and propane. However, they do not support anaerobic metabolism. In addition, if the gases are inadvertently supplied at concentrations that result in the microbial depletion of the available oxygen, undesirable byproducts such as foul-smelling organics, soluble iron, or hydrogen sulfide should not be produced. The disadvantage to enriching for specialized populations using gaseous aliphatic hydrocarbons is the explosion hazard of the hydrocarbons mixed in air at unsafe concentrations. One constraint on *in situ* restoration programs is that the reagents must be dissolved in the perfusion water to reach the zone of contamination; hydrocarbons and the oxygen required for their metabolism are not very soluble in water.

Wilson and White²¹¹ developed a general relationship that may be used to predict the extent of removal of a chlorinated organic as a function of the metabolism of a given amount of hydrocarbon feedstock. The relationship is as follows

$$C/C_o = e^{-kh}$$
(2)

where C = the final concentration of the halogenated organic to be co-oxidized; $C_o =$ the initial concentration of the halogenated organic; h = the amount of hydrocarbon feedstock to be consumed; and k = a utilization constant.

At present, there are limited data available to calculate utilization constants and the generality of the relationship has not been widely tested. The equation may prove to be a powerful tool in the engineering design of *in situ* biorestoration programs. Some utilization constants for trichloroethylene exist.²¹¹ As a paper exercise, the extent of removal of trichloroethylene at a number of critical engineering limitations, including the solubility of methane, propane, and pure oxygen (24, 62, and 40 mg/ ℓ , respectively) and the oxygen content of well-oxygenated ground water (taken to be 8 mg/ ℓ) was estimated. Equation 2 was used to estimate the concentration of trichloroethylene that could be brought down to 5 $\mu g/\ell$, the maximum contaminant level proposed under the Safe Drinking Water Act.²¹² To preview the economics of *in situ* biorestoration, costs of the primary hydrocarbon feed-stock were estimated at 25¢/kg and the cost of oxygen supplied as hydrogen peroxide was estimated at 400¢/kg oxygen supplied.

The predictions of trichloroethylene degradation by populations supported on gaseous aliphatics using Equation 2 are illuminating (Table 8). At ambient oxygen concentrations, the reduction in the concentration of trichloroethylene supported on either propane or methane is environmentally insignificant. The reductions supported by saturating concentrations of oxygen will probably be useful but not sufficient to treat most contaminated water in one cycle: the water will have to be circulated and reinjected with oxygen a number of times, or the oxygen will have to be supplied as hydrogen peroxide. Propane is about three times more soluble in water than methane, and considerably greater removals of trichloroethylene are possible using aropane as the feedstock. Finally, the cost of trichloroethylene biorestoration *in situ* can probably be attributed to the cost of supplying the oxygen.

The quantities of methane and propane are calculated from the equation of Wilson and White.²¹¹ assuming utilization constants for trichloroethylene of 0.075 ℓ water treated per milligram methane consumed and 0.10 ℓ water treated per milligram propane consumed, and assuming utilization constants for *cis*- and *trans*-1.2-dichloroethylene of 0.3 ℓ water treated per milligram methane consumed.

Vinyl chloride and *cis*- and *trans*-1.2-dichloroethylene commonly occur in ground water contaminated with trichloroethylene and probably result from the reductive dechlorination

Table 8

ESTIMATED QUANTITIES OF OXYGEN AND METHANE OR PROPANE REQUIRED TO BRING THE CONCENTRATION OF TRICHLOROETHYLENE, cis- OR trans-1,2-DICHLOROETHYLENE OR VINYL CHLORIDE TO 5 μg/ℓ

Initial	conc*	M re	ethane quired	Ргорал	e required	Oxyger	ı required
TCE (μg/ί)	DCE or VC (µg/{)	mg/ℓ	Cents/ 1000 gal (3785 ()	mg/(Cents/ 1000 gai (3785 ()	mg∕€	Cents/ 1000 gal (3785 ()
2.500				62	5.9	230	340
1.000				53	5.0	190	290
250				39	3.7	140	210
100				29	2.7	105	159
30		24	2.5			96	146
17				11	1.0	40	
11		10	0.9			40	
7				2.2	0.2	8	
5.8		2.0	0.2			8	
5.0						0.0	
	6.700	24	2.5			96	146
	1.000	18	1.7			71	107
	100	10	0.9			40	
	9 .	2	0.2			8	
	5.0	0.0				0.0	

TCE = trichloroethylene; DCE = dichloroethylene; VC = vinyl chloride.

of trichloroethylene.²¹⁴ Utilization constants for these compounds are not available. Wilson and White²¹¹ estimated from the data of Fogel et al.²⁰⁷ that the constants are >0.3 ℓ water treated per milligram methane consumed. Unpublished data of Henson²⁷² suggest that constants for *cis*- and *trans*-1,2-dichloroethylene are >0.8 and 0.4 ℓ water treated per milligram methane consumed, respectively. These higher utilization constants make aquifers contaminated with these compounds much better candidates for *in situ* biorestoration (Table 8). Hydrogen peroxide will probably not be required to achieve adequate treatment. If the contaminated water is pumped to the surface for treatment, the limited solubility of oxygen becomes much less of a problem. The water can be exposed to any desired volume of air in a fixed film bioreactor.²¹¹

Table 9 summarizes the prospects for biorestoration of aquifers contaminated with specific halogenated compounds. These data were compiled by comparing the relative rates of degradation of these compounds in a variety of experimental systems to the rates of transformation of trichloroethylene and *cis*- and *trans*-1,2-dichloroethylene, then assessing the rates in light of the relationships portrayed in Table 8. Prospects are rated "good" if hydrogen peroxide will not be required, "fair" if hydrogen peroxide is required, and "poor" if environmentally insignificant removals cannot be attained with or without hydrogen peroxide.

The relationship of Wilson and White²¹¹ does not presuppose an upper limit on the concentration of the chlorinated contaminant; however, an upper limit obviously exists and toxicity effects have frustrated research in this area. Workers at both Stanford University and R. S. Kerr Environmental Research Laboratory have isolated mixed microbial populations from nature that could degrade trichloroethylene, only to lose the ability to degrade the compound when the primary alkane oxidizer was isolated in pure culture. It is tempting to conclude that the trichloroethylene degrader is not an alkane oxidizer. However, other

Table 9PROSPECTS FOR TREATMENT OF THE COMMON HALOGENATEDORGANIC CONTAMINANTS IN AQUIFERS THROUGH CO-
OXIDATION SUPPORTED ON GASEOUS ALKANES

Compound	Pump	Treat in the		
Compound	and treat	aquiter	Ref.	
Tetrachloroethylene (PCE)*		None	207, 209, 213	
Trichloroethylene (TCE)	Good	Fair	206, 207, 209, 211, 213	
cis-1,2-Dichloroethylene		Good	207, 209, 213	
trans-1,2-Dichloroethylene		Good	207, 209, 213	
Vinyl chloride		Good	207, 215	
Direct utilization may be possible				
1,1-Dichloroethylene		Fair	207	
Carbon tetrachloride*		None	209, 213	
Chloroform		Poor	208, 209, 213	
Methylene chloride		Fair	75, 213	
Direct utilization may be possible	_	_		
1,1,1-Inchloroethane (ICA)	Poor to	Poor	209, 211, 213	
	good			
1,1,2-Trichloroethane (TCA)		Poor	209, 213	
1,1-Dichloroethane (DCA)		Poor	209, 213	
1,2-Dichloroethane		Poor	204, 209, 213, 216	
Direct utilization may be possible				
1,2-Dibromoethane (EDB)		Fair	209, 213	
Direct utilization may be possible				

Removal of carbon tetrachloride and tetrachloroethylene seen in the soil exposed to natural gas is probably an anaerobic process and not a direct result of alkane oxidation.²⁷²

possibilities exist. In certain mixed cultures or microcosms of aquifers, trichloroethylene started to inhibit oxidation of the hydrocarbon feedstock at a concentration of about 1000 $\mu g/\ell$.^{270,271} This is far below concentrations that produce toxicity in ordinary heterotrophs. Perhaps the effective toxicant was trichloroethylene epoxide rather than trichloroethylene itself, and the organism that oxidized the primary hydrocarbon feedstock was protected in mixed populations by other organisms. This toxicity threshold must be more carefully defined to aid in identifying contaminated ground water amenable to biorestoration. This work should be done with mixed cultures or microcosms, using systems that simulate the conditions in the subsurface environment.

No technique to remediate environmental contamination is universally applicable. However, there should be many contamination incidents where biorestoration through a forced co-oxidation is the technology of choice, either alone or in conjunction with physical containment. Successful application of the approach will require adequate understanding of the physiology of the biotransformation and quantitative information on the nutritional ecology of the active organisms.

III. WITHDRAWAL AND TREATMENT

A. Biological Wastewater Treatment Processes

Ground water can be withdrawn and treated by conventional biological wastewater treatment processes. Treatment processes used to treat contaminated ground water and leachate from hazardous wastes include (1) suspended growth processes such as activated sludge, lagoons, waste stabilization ponds, and fluidized bed reactors; and (2) fixed film processes such as trickling filters, rotating biological discs, sequencing batch reactors, and others. The wastewater can be treated on site by one of these processes or off site at a municipal or

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commercial treatment plant. A short discussion of each process follows with regard to hazardous waste management. More detailed discussions of these processes are presented in J. R. B. Associates,¹¹³ Ehrenfeld and Bass,¹³⁹ Shuckrow et al.,²¹⁷ Nyer,²¹⁸ and Canter and Knox,²¹⁹.

The most commonly used municipal wastewater treatment process, activated sludge, has a number of advantages for treatment of contaminated ground waters. The units include an aeration basin, a clarifier, and sludge recycle. Following treatment in the aeration basin, a portion of the sludge collected in the clarifier is recycled. The recycling process allows an acclimated microbial population to build up in the system, hence the name activated sludge. The settled sludge can adsorb heavy metals and some organics which may cause the sludge to be considered a hazardous waste.²¹⁷ However, some compounds are removed by volatilization during the aeration step.²²⁰ Activated sludge treatment can reduce the soluble biochemical oxygen demand (BOD) to <10 mg/ ℓ and the total BOD, including suspended solids, to <30 mg/ ℓ . The retention time is short and consequently the process is sensitive to toxic and hydraulic shocks. A survey of 92 industrial wastewater streams conducted by the EPA reported mean BOD removal efficiencies of 86%.¹³⁹ Specific organic compounds can be degraded to low levels; effluent levels of phenol as low as 0.02 mg/ ℓ have been reported.²¹⁸

The sequencing batch reactor is an application of the activated sludge process which may be used to treat hazardous waste leachates.²²¹ The process involves five steps per cycle: (1) fill — the wastewater is drawn into the vessel where some of the activated sludge from the previous cycle remains; (2) react — aeration and mixing occur; (3) settle — clarification occurs in this step; (4) draw — the supernatant is withdrawn; and (5) idle — the system remains idle until the next cycle is initiated. Treatment of hazardous waste with the sequencing batch reactor may be advantageous because the process is more complete and flexible than other treatment technologies and can provide intermittent treatment; in addition, the same tank can be used for both treatment and clarification. Up to 90% of the TOC from a hazardous waste leachate was removed under a 24-hr cycle with a 10-day retention time.

Like activated sludge, surface impoundments such as aerobic lagoons, facultative lagoons. anaerobic lagoons, and waste stabilization ponds rely on suspended microbial populations to degrade organic material; unlike activated sludge, the biomass is not recycled.^{139,222} Even though the processes typically require less energy and supervision than activated sludge, the operational controls are not as flexible.²¹⁷ The retention time of waste in a surface impoundment is often on the order of weeks, whereas that of activated sludge may take a few hours. In general, surface impoundments are quite large, and their size allows for dilution and buffer fluctuations in organic load. Aerobic lagoons are aerated mechanically or by diffusion to increase the degradation rate of organic material and mix the system. 139,220 Organic material is degraded aerobically at the surface and anaerobically near the bottom of facultative lagoons.¹³⁹ Because aeration is not forced or used, facultative and anaerobic lagoons offer the advantage of easy operation and low cost; ²¹⁷ however, anaerobic processes result in incomplete degradation of organic compounds and hence low-quality effluent. Facultative lagoons can also tolerate higher organic loading than aerobic lagoons and both facultative and anaerobic lagoons may generate noxious odors.²²⁰ Anaerobic processes are enhanced in anaerobic lagoons by low surface-to-volume ratios.¹³⁹ Waste stabilization ponds are lagoons that are aerated by natural processes such as wind and photosynthesis. The ponds are principally a polishing technique for low organic waste waters. The ponds are usually 0.3 to 0.6 m in depth. Removal efficiencies for surface impoundments are in the range of 60 to 90%. They are sensitive to shock loadings of toxic chemicals and fluctuations in temperature.

Fluidized bed reactors are filled with materials such as sand or coal that are suspended by wastewater which flows upward through the material.²²² The particles are colonized by a dense growth of microorganisms which rapidly degrade organic material present in the waste stream.

In the fixed film process, wastewater is passed over a surface colonized with microorganisms; the attached biofilm degrades the organic material. The original fixed film process, the trickling filter, uses a solid medium such as rock or plastic as the surface for microbial attachment.²¹⁹ Trickling filters can remove from 60 to 85% of the BOD.²²⁰ Suspended or colloidal organics can be treated, and the process is usually limited to low organic loadings.¹¹³

Trickling filters that are operated anaerobically are known as anaerobic filters.²²⁰ The anaerobic filter process can tolerate high loading rates. Low pH and inorganics such as sodium, sulfate, and heavy metals may inhibit methanogenesis and toxic organics may also be a problem.⁸⁴ The biological tower is another variation of the trickling filter. The tower is packed with a colonizable surface which may reach a height of 4.9 to 6.1 m.²¹⁹ The process operates in a countercurrent mode; contaminated water is sprayed on the top of the tower as air is pulled from the bottom.

A rotating biological disc is similar in concept to trickling filters. Discs or drums which are coated with a biofilm are partially submerged and rotated through the wastewater.^{139,222} Rotation of the discs aerates the attached biofilm. The process is sensitive to shock loading and temperature fluctuations but otherwise is moderately reliable.¹¹³ In comparison to activated sludge, rotating biological discs require less energy and are easier to operate, but are similar in effectiveness.²²⁰ Clarification may be required before and after treatment of wastewater with rotating biological discs.¹³⁹

Biological wastewater treatment processes may be used to treat the following classes of organic compounds typically found in ground water: alcohols, organic acids, aldehydes, ketones, quinones, amines, amides, carbohydrates, esters, some ethers, phenolics, and some aromatics.^{220,223} Compounds that may be difficult to treat with biological wastewater processes include halocarbons, high molecular weight polynuclear aromatics, pesticides, and organometals.¹³⁹

B. Examples of Withdrawal and Biological Treatment

Biological wastewater treatment processes have been used in remedial action at several hazardous and nonhazardous waste sites. Adequate treatment of leachates from recent municipal refuse landfills that contained high levels of free fatty acids was achieved by biological treatment.²²⁴ Leachates from older landfills may be more amenable to physical-chemical treatment processes. In a pilot study. Stover and Kincannon²²⁵ were able to decontaminate ground water from a hazardous waste site using activated sludge. The batch-activated sludge pilot system was seeded with organisms that were acclimated to the same compounds found in the contaminated ground water — phenols, cresols, dichlorobenzenes, and others. Following acclimation and stabilization of the batch-activated sludge for 3 weeks, the organisms were able to reduce the total phenols, TOC, BOD, and COD by 80% or more within 24 hr.

C. Combinations of Biological Treatment with Other Processes

Combination of conventional biological wastewater treatment with other water treatment processes such as GAC, air stripping, and addition of acclimated bacteria have also been successful. Feasibility studies on decontamination of leachate from the Ott/Story hazardous waste site in Muskegon, Mich., have combined activated sludge and GAC adsorption to remove various halogenated aliphatics, benzene, and toluene.²²⁶ Initial attempts to acclimate an activated sludge culture to the organic contaminants were minimally successful and the addition of a commercial microbial culture was not effective; however, a combination of GAC adsorption followed by activated sludge removed >95% of the TOC. The activated sludge organisms removed the organics that were not sorbed in the GAC treatment. Treatment efficiencies were >75% as long as the removal efficiency of the GAC was high. Anaerobic treatment combined with GAC was less effective than aerobic treatment (activated sludge) and suffered the same decline as the aerobic process when the GAC was saturated.²¹⁷ Removal

of TOC by a treatment train using GAC followed by anaerobic and then aerobic biological treatments was also tested.²²⁷ The biological treatment steps were not necessary when the GAC sorption sites were not significantly saturated; however, the biological treatment increased the removal efficiency of the treatment train as more GAC sorption sites became saturated. The TOC removal efficiency of GAC combined with anaerobic and aerobic treatment was less than that of GAC and aerobic treatment only.

Josephson⁶⁷ reported that a combination of powdered activated carbon and activated sludge was used to treat ground water contaminated with hydrocarbons, pesticides, and other organics. A removal efficiency of 95 to 99% was achieved for the COD, total nitrogen, and various organics.

Air stripping followed by biological treatment was used in a pilot study to treat ground water contaminated with trichloroethylene, freon. 1,2-dichloroethene, toluene, ethyl benzene, xylenes, vinyl chloride, acetone, isopropanol, o-dichlorobenzene, 1,1-dichloroethylene, and 1,2-dichlorophenol.^{22#} Air stripping could remove all of the organics except for the nonvolatile compounds isopropanol and acetone; however, a treatability study indicated that the nonvolatile compounds were biodegradable. Hence, a treatment system utilizing both air stripping and biological treatment was recommended for this site.

Nyer and Sauer²²⁹ described the cleanup of shallow ground water from a Gulf Coast hazardous waste site. The saline aquifer was contaminated with 400 mg/ ℓ phenol and other organics which resulted in a TOC concentration of 1300 mg/ ℓ . Several options that were considered for treatment are reported with estimated costs per gallon in parenthesis: pond evaporation with oxygen and nutrient addition (\$0.028); deep well injection (\$0.183); so-lidification/adsorption to concentrate the liquid and then adsorb the material to trench backfill (\$0.085); GAC adsorption (\$0.058); biological treatment (\$0.005).

A feasibility study indicated that the organics were biodegradable, but carbon adsorption would be required as a polishing technique.²²⁹ The overall treatment system would consist of: (1) pH adjustment: (2) chemical addition: (3) biological treatment with two aeration basins, a clarifier, and a fixed activated sludge treatment system (FAST): (4) filtration through a dual media filter: and (5) carbon adsorption. The FAST system uses particles of plastic colonized by bacteria in a well-mixed tank. The system is essentially a hybrid of activated sludge from a refinery that treated ballast from oil tankers. Results from the pilot plant, which included the aeration plant and clarifier only, indicated that the TOC was reduced by 70%. Addition of the FAST system, the dual media filter, and the carbon adsorption unit to the treatment train reduced the concentration of TOC from 1300 to 18 mg/ ℓ (98%).²¹⁸

Addition of mutant bacteria to a sequencing batch reactor, a process patented in 1985 by Colaruotolo et al.,²³⁰ was used to treat leachate collected from the Hyde Park Landfill in Niagara Falls, N.Y.²²¹ The leachate contained chlorinated organics, phenol, and benzoic acid. A consortium of microorganisms that could degrade most of the contaminants was isolated from the leachate; however, degradation of the pollutants by bacterial strains in the consortium was variable.²³¹ By genetic manipulation, organisms in the consortium that could degrade the remaining compounds were found. Tests with bench-scale sequencing batch reactors and also pilot-plant scale units indicated that the TOC was reduced by 85% or greater and that individual contaminants were generally reduced by 95% or greater. The biomass yield was 0.64 mg/mg feed TOC. Amendments of nitrogen and phosphorus did not improve treatment over the addition of only nitrogen. Cost savings for the biological treatment over the existing carbon adsorption system were estimated to range from \$538,000 up to \$783,000.

Bartha²³² suggested that inoculation of microorganisms into a wastewater treatment process should be judged with caution. Inoculation may be useful for startup, disruptions, for certain xenobiotics that cannot be degraded by the natural flora, or when the added organisms cannot sustain themselves.

IV. HYDROLOGIC CONSIDERATIONS AND MATHEMATICAL MODELING OF BIORESTORATION

A. Hydrologic Considerations

A number of methods have been reported in the literature for the containment of contaminated ground water through hydraulic control or through injection-pumping networks of wells. Biorestoration of a contaminant plume may involve the addition of nutrients such as dissolved oxygen or hydrogen peroxide or the addition of microbes capable of degrading a particular waste. In order for such additions to be successful, it may be necessary to use hydraulic controls to minimize the migration of the plume during the *in situ* treatment process. Thus, hydrologic considerations cannot be neglected in the biorestoration of aquifers.

Hydraulic control methods depend to a large extent on variability of aquifer hydraulic conductivities, background velocities, and sustainable pumping rates. Typical patterns of wells which are used to provide hydraulic controls include (1) the injection-production pair, (2) a line of downgradient pumping wells, (3) a pattern of injection-production wells around the boundary of a plume, and (4) the "double-cell" hydraulic containment presented by Wilson.²³³ Well systems can also be used to capture and withdraw entire zones of contaminated water for treatment above ground.

Analytical equations and graphical solutions are available for estimating flow rates and limits of hydrodynamic isolation under various boundary conditions. Numerical computer models of ground water flow and contaminant transport are required when site geology is complex, heterogeneous, and anisotropic. A simple hydrodynamic isolation system within a uniform flow field involves the placement of a recharge well of the same strength upgradient from a pumping well. Standard equations describe the head h(x,y) as a function of pumping rate, ambient flow rate, and transmissivity of the aquifer. The region of recirculation which connects the stagnation points can be evaluated and provides a measure of the capture zone of contaminated ground water.²³⁴

Wilson²³³ presents a "double-cell" hydraulic containment system which utilizes an inner cell and an outer recirculation cell, with four wells along a line bisecting the plume in the direction of flow. The method is more efficient in terms of flushing times and recirculation rates than the single cell. The double-cell method provides added flexibility and a back-up system if pumps should fail in either system.

Ozbilgin and Powers²³⁵ described hydrodynamic isolation systems for several EPA hazardous waste sites. Pumping wells and an upgradient recharge trench were successful in retarding the advance of a contaminated plume at the site in Nashua. N.H. They concluded that hydrodynamic isolation systems are generally less costly and time consuming than physical containment structures such as slurry walls. Well systems are more flexible in that pump rates and well locations can be altered as the system is operated over a period of time.

Shafer²³⁶ indicated that pumping-injection systems can be used (1) to create stagnation (no flow) zones at precise locations in a flow field, (2) to create gradient barriers to pollution migration, (3) to control the trajectory of a contaminant plume, and (4) to intercept the trajectory of a contaminant plume. However, the determination of pumping rates to achieve a pollution control objective can be difficult. Thus, investigators have explored the application of outpinization theory to determine optimal pumping rates for creation of hydraulic controls,

Gorelick²³⁷ and Atwood and Gorelick²³⁴ focus on using linear programming (LP) methods to determine the best containment strategy in combination with a ground water flow simulator. From a specified set of potential well sites, the model approach selects well locations and optimal pumping/recharge rate schedules to contain the contaminant plume. Shafer²³⁶ advocates the use of nonlinear programming combined with a ground water flow model and an advective transport model. The optimization method is applied to examples for determining stagnation points in a flow field and for steering the trajectory of a contaminant plume. Optimization methods offer more efficient solutions than the typical trial and error approaches

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for exploring cleanup strategies. However, nonlinear programming requires the flow and transport models to run during each iteration in which new pumping rates are selected and tested in the overall performance index or objective function. In the present case, optimization methods are complex and time consuming and may not offer any improvements over simulation for the complex case of biorestoration alternatives.

Successful biorestoration alternatives at a particular site depend on the hydrological and geological characteristics of the aquifer. If the contaminant plume is moving rapidly through a sandy-gravelly zone, then hydraulic controls may be required to halt the advance of the plume and to provide injection points for added nutrients or oxygen. Pumping out ground water and surface nutrient additions prior to reinjection may provide a more controlled input to the biorestoration process.

For the case of slowly moving organic plumes in a silty sand aquifer, it may be hydrologically difficult to pump or inject recharge waters at rates greater than 19 or $38 \ell/\min$. In such cases, large numbers of wells may be needed to provide better "hydraulic spreading" of treated recharge water. Simple lines of wells upgradient or downgradient of the plume may not provide the required circulation, and wells within the plume are usually needed. A five-spot pattern (one injection surrounded by four pumping wells) provides a useful network for many cases.

In summary, hydraulic controls for the containment of ground water should be carefully considered for any site where biorestoration is a viable treatment alternative. In particular, injection-pumping well networks offer advantages for the creation of stagnation (no-flow) zones or for the control of the trajectory of a contaminant plume. Once the plume has been controlled hydraulically, then application of additional nutrients, oxygen, or microbes can be better controlled and evaluated in terms of biodegradation efficiency.

B. Modeling Biorestoration

Mathematical modeling of biorestoration processes is useful in simulating cleanup progress and can provide insights into the kinetics of the restoration process. Modeling of the hydraulics of the site may also aid in designing the optimum injection and production system. Development of mathematical models of the biorestoration process requires: (1) a description of the kinetics of biodegradation/transformation in the subsurface, (2) a description of the abiotic processes controlling the transport and availability of the contaminant and other required nutrients, and (3) an appropriate procedure for combining the processes and predicting the effect of the biorestoration technique. Most attempts at quantifying the transport and removal of contaminants in ground water have relied on a solution of the classical form of the advection-dispersion equation. The general form of this equation is

$$\frac{\partial C}{\partial t} = \nabla \cdot (\widetilde{D} \nabla C - vC) + \Sigma R_{i}$$
(3)

where C = contaminant concentration, t = time, v = velocity vector, \widetilde{D} = dispersion tensor, R_i = chemical and biological reaction terms, and ∇ = the del operator.

Solutions to this equation have been obtained using a variety of analytical and numerical methods. Thorough reviews of these methods may be found in Anderson.²³⁹ Bear.²³⁴ and Javandel et al.²⁴⁰ In this section, mathematical descriptions of biodegradation kinetics are reviewed along with commonly used descriptions of abiotic transport processes. Commonly used techniques for solving these equations are then reviewed as well as some of the advantages and disadvantages of mathematical modeling.

C. Kinetics of Biodegradation

In situ biorestoration usually involves the addition of electron acceptors and nutrients to enhance the growth of micoorganisms present in the subsurface and consequently increase

the rate of contaminant biodegradation. In order to model the degradation process, relationships are needed which describe the kinetics of microbial growth and consumption of added nutrients and electron acceptors. These relationships are then combined with Equation 3 to describe the movement and consumption of the contaminant and added nutrients. One of the most popular relationships for describing the growth and decay of microorganisms and consumption of organic substrate was originally proposed by Monod²⁴¹ and modified by Herbert et al.²⁴² This model takes the following form:

$$\frac{dX}{dt} = \mu XY \frac{S}{K+S} - bX$$
(4)

and

$$\frac{dS}{dt} = \mu X \frac{S}{K+S}$$
(5)

where X = microbial concentration (mg/ℓ) , μ = maximum specific utilization rate (1/day), Y = microbial yield coefficient (g/g). S = limiting substrate (mg/ℓ) , b = microbial decay rate (1/day), and K = substrate half-saturation constant (mg/ℓ) .

Growth is assumed to be a hyperbolic function of some limiting nutrient. Microbial decay is assumed to be a constant independent of other environmental conditions. When several compounds are used simultaneously, Equation 4 can be modified as

$$\frac{dX}{dt} = \mu Y X \frac{C_1}{K_1 + C_1} \frac{C_2}{K_2 + C_2} \frac{C_3}{K_3 + C_3} \cdots \frac{C_n}{K_n + C_n} - bX$$
(6)

where $C_i = \text{limiting nutrient i}$ and $K_i = \text{substrate half-saturation constant for nutrient i}$. When $C_i \ge K_i$, the function $(C_i/K_i + C_i)$ goes to 1 and has no effect on the growth of the microorganisms, but when $C_i \ll K_i$, the growth rate will be directly proportional to the concentration of nutrient i. These equations also predict that as the concentration of nutrient i decreases, the net growth rate will approach zero and eventually become negative. For a i decreases, the net growth rate will approach zero and eventually become negative. For a population to survive, the long-term growth rate must be greater than or equal to zero; population to survive, the long-term growth rate must be greater than or equal to zero; population to survive, the long-term growth rate must be greater than or equal to zero; population to survive, the long-term growth rate must be greater than or equal to zero; population to survive, the long-term growth rate must be greater than or equal to zero; population to survive, the long-term growth rate must be greater than or equal to zero; population to survive, the long-term growth rate must be greater than or equal to zero; population to survive, the long-term growth rate must be greater than or equal to zero; population to survive, the long-term growth rate must be greater than or equal to zero; population to survive, the long-term growth rate must be greater than or equal to zero; population to survive, the long-term growth rate must be greater than or equal to zero; population to survive, the long-term growth rate must be greater than or equal to zero; population to survive, the long-term growth rate must be greater than or equal to zero; population to survive, the long-term growth rate must be greater than or equal to zero; population to survive, the long-term growth rate must be greater than or equal to zero; population to survive, the long-term growth rate must be greater than or equal to zero; population to survive, the long-term growth rate must be greater than

(C_{min}) where

$$C_{\min} = \frac{K_i b}{\mu Y - b}$$
(7)

This equation suggests that microorganisms may not be capable of degrading organic contaminants below this concentration. McCarty¹⁵³ has suggested the addition of a second nonharmful substrate to support the growth of the organisms and allow degradation to below C_{min} , although addition of a more readily degradable substrate could suppress the degradation of the contaminant of interest. Yoon et al.²⁴³ have presented a mathematical model for simulating growth of a mixed microbial population on multiple substrates. For two substrates:

$$\frac{dX}{dt} = \mu YX - bX$$
(8)

where

$$\mu^{*} = \frac{\mu_{m_1}S_1}{K_1 + S_1 + \alpha_2S_2} + \frac{\mu_{m_2}S_2}{K_2 + S_2 + \alpha_1S_1}$$
where $S_{1,2}$ = substrates 1 and 2, $K_{1,2}$ = half-saturation constants for substrates 1 and 2, $\mu_{m1,m2}$ = maximum specific utilization rates for substrates 1 and 2, and $\alpha_{1,2}$ = inhibition constants. This model can be further extended to describe growth on multiple substrates.

Some contaminants will not be used as a carbon and energy source by the microorganisms but are transformed. Schmidt et al.²⁴⁴ have shown that transformation of these compounds is proportional to microbial population and contaminant concentration (C) where

$$\frac{dC}{dt} = -KXC$$
(9)

Schmidt et al.²¹⁴ used a logistic curve to describe the change in microbial concentration in a batch system and developed a series of equations for describing change in contaminant concentration with time for differing initial microbial and contaminant concentrations. Use of the logistic curve greatly simplifies the mathematical computations but does not allow simulation of the effects of changing aquifer parameters such as the addition of a second substrate. In aquifer restoration, simulation of the microbial population using Equation 4 and change in contaminant concentration by Equation 9 may provide a more useful prediction.

Various workers have suggested that the kinetics of microbial growth, decay, and consumption of organic contaminants in the subsurface are best described by models which include terms for transport into attached biofilms or microcolonies. It is well known that most microorganisms in the subsurface are attached to soil particles.¹⁰ This is thought to be due to the competitive advantage attachment gives a microorganism at low substrate concentrations.²⁴⁵

Workers at Stanford University have developed a series of models for simulating degradation of organics in biofilms. The basic model assumes that degradation within the biofilm can be described by Monod kinetics. Mass transport into the biofilm is by diffusion alone. The diffusive flux (J) is calculated from Fick's second law

$$J = -D \frac{dS_f}{dz}$$
(10)

where $S_r = \text{concentration}$ of rate-limiting substrate, z = coordinate orthogonal to biofilm, and D = diffusivity. Different diffusivities are assigned to the biofilm and an effective diffusion layer adjacent to the biofilm. Williamson and McCarty²⁴⁶ originally developed this model to simulate either substrate or oxygen limited biodegradation in wastewater treatment biofilms. Rittman and McCarty²⁴⁷ modified this approach to describe the steady-state biofilm surrounding an injection well receiving tertiary-treated wastewater. Bouwer and McCarty²⁴⁸ have further expanded the approach to allow simulation of secondary utilization of trace organics while the biofilm is supported by an undifferentiated COD. Most recently, Kissel et al.²⁴⁹ have employed the biofilm concept to model carbonaceous oxidation, nitrification, and denitrification within a mixed culture biofilm.

Much of the work on biofilms at Stanford occurred as an outgrowth of field studies on organic degradation near an injection well. In this region, substrate fluxes and ground water velocities will be high and a biofilm can be expected to develop. Actual biofilms are rare in most aquifers and the majority of the microorganisms are present as microcolonies. Molz et al.²⁵⁰ have recently modified the biofilm concept to describe the growth and decay of microorganisms present in microcolonies. An average colony radius and thickness is used to describe the microcolonies. Growth and Jecay within the colony is simulated by Monod kinetics and includes both oxygen and substrate limitation. Transport to the microcolony is limited by a diffusion layer at the colony surface.

D. Modeling Subsurface Transport

Keely et al.²³¹ present a concise overview of evolving concepts of subsurface contaminant transport. They argue that state-of-the-science methods may cost more at the outset but may

yield overall benefits in the form of reduced cleanup costs compared with conventional methods. The authors make the point that ground water processes are difficult to understand and to model due to interactions which may not be simple to describe. Biotransformation in the presence of dissolved oxygen in an aquifer represents an example where research results may pave the way for reduced cleanup costs at many sites. If more detailed data can be obtained about potential pathways and mechanisms of transport, the state of the art will be advanced along with the potential for less costly site restoration.

The major physical processes of importance in ground water transport are advection and dispersion.²⁵² Advection is the transport of a contaminant by the bulk ground water flow. Dispersion is the spreading of a contaminant front due to molecular diffusion and small-scale variations in fluid velocity throughout the aquifer.

The major chemical processes of interest are adsorption, ion exchange, hydrolysis, and oxidation-reduction reactions. Adsorption is "the process in which matter is extracted from the solution phase and concentrated on the surface of the solid material."²⁵³

1. Dispersion

Dispersion, the spreading of a contaminant front as it moves in the ground water, is an area of particular controversy at this time. The dispersion process can be most easily described as consisting of three components: (1) molecular diffusion resulting from Brownian motion of individual molecules, (2) hydrodynamic dispersion resulting from variations in interstitial pore velocities, and (3) macrodispersion resulting from structural variations in hydraulic conductivity and, consequently, velocity. Differences in permeability between layers can result in different ground water velocities and large variations in solute concentration. When an aquifer is monitored using a fully screened well, ground water from different layers is mixed, resulting in a smoothing of the apparent solute breakthrough curve. This smoothing can result in very large apparent dispersion when matched against simple two-dimensional solute transport models.

The effects of molecular diffusion, hydrodynamic dispersion, and macrodispersion are frequently combined to form a dispersivity tensor which in some cases can be reduced to three main components: longitudinal dispersivity (a_i) , transverse dispersivity (a_i) , and vertical dispersivity (a_i) .

Dispersion coefficients (D) used in the advection dispersion equation are found by

$$\mathbf{D} = \mathbf{a}\mathbf{v}^m \tag{11}$$

where v is the resultant velocity scalar and m is assumed equal to 1.

The physics and mathematics necessary to describe molecular diffusion and hydrodynamic dispersion are well established. Bear²³⁴ and Fried²⁵⁴ provide comprehensive experimental and theoretical reviews of these processes. The significance of the third component, macrodispersion, is the subject of much debate. Anderson²⁵⁵ summarizes much of the current research on the nature and significance of macrodispersion. At present, there appear to be two dominant approaches:

- 1. Macrodispersion occurs due to random variations in permeability which can never be adequately characterized; consequently, the only reasonable method is to employ a stochastic procedure for describing the average movement of a solute.
- The apparent spreading of many solute fronts is due to variations in permeability which are complex but measureable: consequently, more effort should be expended towards measuring the actual permeability distributions and using these as input for deterministic simulations.

No work has yet been focused on the effect of varying aquifer parameters on solute transport as it relates to biorestoration. At present, the predictive accuracy of biorestoration modeling is severely limited by uncertainties in solute transport simulations. When simulating the transport of a contaminant and oxygen or other nutrient, the most commonly used numerical models will predict significant mixing between the contaminants and oxygen and high rates of biodegradation. In real aquifers, contaminants may be trapped in a few areas of low permeability while the oxygen or other nutrients are forced through the high-permeability zones. In this situation, little mixing of the contaminants and oxygen will occur, and consequently, little biodegradation. Until solute transport models are developed which can adequately describe the complexities of subsurface flow, the accuracy in which biorestoration can be simulated will be limited.

2. Chemical Processes

The major chemical processes which affect the transport of organic contaminants in ground water are adsorption and hydrolysis.

Adsorption is a surface process in which a compound "sticks" to the solid aquifer material. In the case of neutral, nonpolar organics, this stickiness is due to the much higher affinity of the compound for other organics attached to the soil than for the polar water phase. In the case of polar molecules, adsorption may be due to dipole:dipole forces. The attraction due to this mechanism is typically much weaker than that for hydrophobic compounds.

Naturally occurring organic material in aquifers is commonly present as a humic-kerogen film over the clay particles. This organic material may originate from humic or fulvic acids deposited with the original sediment or from infiltrating rain water. Organic material is effectively preserved in tight clays where diffusion of oxygen is limited and the redox potential is low.

Hydrolysis reactions can have a major impact on the mobility of organic compounds in aquifers. These reactions are typically pH dependent and catalyzed by metal ions. The pH of most solutions will approach equilibrium shortly after entering an aquifer. In this case, hydrolysis reactions can be modeled as a simple first-order decay process.

When attempting to develop models for simulating the adsorption of contaminants in ground water, many early investigators assumed that at low concentrations contaminants move independently of other solutes, the reaction kinetics are fast relative to ground water flow, and the natural reactants are uniformly distributed throughout the aquifer. These assumptions allow the reactions to be analyzed using the equilibrium isotherm approach. Under this approach, the variation in adsorbed contaminant concentration is described by an adsorption isotherm:

$$\mathbf{S} = \mathbf{f}(\mathbf{C}) \tag{12}$$

where C = concentration of the contaminant in solution and S = concentration in the nonmobile solid phase. This relationship can be incorporated into the advection dispersion equation by considering the loss of solute to adsorption.

If S is a linear function of C, then the effect of adsorption can be replaced by a constant retardation factor (R). In this special case, the adsorbed contaminant will move according to Equation 2 with an effective velocity, v', where v' = v/R and an effective dispersion coefficient, D' = D/R. A common method of calculating R is by the relation²⁵²

$$\mathbf{R} = \mathbf{I} + \rho \, \mathbf{K}_{\mathbf{u}} / \mathbf{n} \tag{13}$$

where n is the aquifer porosity, ρ the bulk density, and K_d the partition coefficient in grams of contaminant adsorbed per gram aquifer.

The use of a retardation factor depends on the following assumptions:

1. Adsorption can be described by a linear relationship between solute and solid phase concentration.

- 2. The reaction kinetics are fast relative to ground water flow.
- 3. Natural reactants attached to the aquifer material can be assumed uniformly distributed in space.
- 4. Contaminant transport is independent of other liquid phase organics.

E. Mathematical Models of Subsurface Biorestoration

Equation 3 with terms included for biodegradation can be solved to obtain the concentration of the contaminant in space and time by both analytical and numerical methods. Analytical solutions generally require less effort for the model user to employ, but may also require simplification of the aquifer conditions and biodegradation processes. For uniform flow in an aquifer in which biodegradation may be approximated as a first-order decay, solute concentrations in space and time can be calculated using the one-dimensional solution of Ogata and Banks²⁵⁶ or the two-dimensional solution of Wilson and Miller.²⁵⁷ Approximating biodegradation as a first-order decay would be appropriate when the microbial concentration is constant, growth is only dependent on the contaminant concentration, and the contaminant concentration is significantly less than the half-saturation constant (K). Simkins and Alexander²⁵⁸ provide useful guidelines for determining when consumption of substrate may be approximated as a first-order decay.

Numerical solution of Equation 3 allows the user much more flexibility in specifying aquifer geometry and biodegradation kinetics. The most common mathematical formulations for approximating the solute transport equation are finite differences, finite elements, and the methods of characteristics.

Finite difference models have been developed for a variety of field situations including saturated and unsaturated flow and for transient and constant pollutant sources. Finite difference methods operate by dividing space into rectilinear cells along the coordinate axes. Homogeneous values within each cell are represented by values at a single node. Partial differentials can then be approximated by finite differences and the resulting set of equations solved by iteration.^{259,260} Approximating the differentials by a difference requires that the remaining terms of the Taylor's expansion be dropped, resulting in a truncation error and significant spreading of the simulated contaminant front. This spreading has been termed numerical dispersion and can often mask the actual physical dispersion process.²¹⁹

The finite element method also operates by breaking the flow field into elements, but in this case the elements may vary in size and shape. In the case of a triangular element, the geometry would be described by the three corner nodes where heads and concentrations are computed. The head or concentration within an element is allowed to vary in proportion to the distance to these nodes. Complex interpolating schemes are sometimes used to predict accurately parameter values within an element and thereby reduce the truncation errors common in finite difference procedures. Some numerical dispersion may still occur but is usually much less significant. The use of variable size and shape elements also allows greater flexibility in the analysis of moving boundary problems which occur when there is a moving water table or when contaminant and flow transport must be analyzed as a coupled problem. A disadvantage of the finite element method is the greater mathematical complexity and generally higher computing costs.^{261,262}

The method of characteristics (MOC) is most useful where solute transport is dominated by convective transport. One of the most commonly used models employs a procedure where idealized particles are tracked through the flow field.²⁶³ In step one, a particle and associated mass of contaminant is translated a certain distance according to the flow velocity. The second step adds on the effect of longitudinal and transverse dispersion and sources and sinks for the contaminant.

All of these techniques can be used to simulate *in situ* biorestoration under certain circumstances, although no single procedure will be applicable to every situation. Only very limited work has been done on simulating the simultaneous effects of advection, dispersion, and chemical and biological processes. In the following section, the few studies that have been performed are reviewed and the potential weakness of each technique discussed.

Kosson et al.²⁶⁴ employ a simple one-dimensional finite difference solution to simulate the movement of hazardous industrial wastewaters through an acclimated soil column. Adsorption is assumed to be linear and is described by a retardation factor. A portion of the influent wastewater is assumed nondegradable. Biodegradation of the remainder is simulated as a first-order decay. Experimental data are also provided by a field scale column used to study the degradation process. The model adequately matches experimental data from the later portion of the column biodegradation test when an acclimated microbial population has developed. Agreement between model and experimental results was not as good during the earlier part of the test before the microbial population had reached steady state.

Angelakis and Rolston²⁰⁵ present a mathematical model for simulating the movement of insoluble (particulate) and soluble organic carbon through the unsaturated soil profile. Transformation from insoluble to soluble and finally to carbon dioxide is assumed to follow first-order kinetics. Transport of carbon dioxide is by gaseous diffusion. Simulation results are obtained from analytical and numerical solutions. These results compare favorably with experimental data from a series of column tests performed using primary wastewater effluent. Insoluble and soluble organic carbon distributions were adequately matched. A variable gaseous diffusion coefficient was required to match the observed carbon dioxide distribution.

Baehr and Corapcioglu²⁶⁶ present a one-dimensional model for simulating gasoline transport in the unsaturated zone which includes transport by air, water, and free hydrocarbon phases. The hydrocarbon is assumed to be composed of "n" components of differing solubility and volatility. Exchange between the air, water, hydrocarbon, and adsorbed phases is assumed to be rapid and described by equilibrium partition coefficients. Biodegradation of the hydrocarbon is limited by the availability of oxygen which can enter the soil dissolved in the water phase or by gaseous diffusion. Microorganism growth was not simulated directly since biodegradation was assumed to be rapid relative to mass transport and to be limited by the availability of oxygen. The equations are solved numerically using a finite difference procedure. Model simulations indicated that the rate of biodegradation was very sensitive to the diffusive properties of the soil. No experimental data are presented to test the model predictions.

Sykes et al.²⁶⁷ simulate the anaerobic degradation of a landfill leachate plume in the saturated zone at the Canadian Forces Base in Borden, Ontario. Microbial growth, decay, and substrate utilization are simulated using Monod kinetics. When substrate concentrations are significantly below the half-saturation constant and microbial populations are close to steady state, the biodegradation kinetics are reduced to a first-order decay. The nonlinear equations are generated using a Galerkin finite element approximation and solved using a Newton Raphson iteration procedure. Model simulations indicate that the majority of the degradable organics can be expected to be removed within a few meters of the landfill. This finding was confirmed in field studies at the site. Sensitivity analyses performed using a one-dimensional solution indicated that, under certain circumstances, pulses of organics could escape from the landfill before a significant microbial population had developed.

Molz et al.²⁵⁰ present a numerical model for simulating substrate and oxygen transport and use by attached microorganisms. The microbial population is assumed to be immobile and present in microcolonies of an average thickness and radius. Transport into the microcolonies of oxygen and substrate is limited by diffusion through a stagnant layer adjacent to the microcolony. Microbial growth and consumption of oxygen and substrate within the microcolony is described by Monod kinetics. A one-dimensional solution is obtained numerically using an Eulerian-Lagrangian finite element solution. The numerical model will then be used to simulate the transport and biodegradation of substrate and oxygen in a laboratory column. The simulation results indicate that degradation is most rapid near the column inlet. The initial microbial population has a significant effect on the simulated

breakthrough at the beginning of the simulation but has little effect on the steady-state substrate distribution. Large substrate loadings at the column inlet quickly exceed the available oxygen supply, resulting in anaerobic conditions throughout the majority of the column. Laboratory testing of the simulation model is planned.

Borden and Bedient¹⁴⁰ present a numerical model of oxygen-limited biodegradation of hydrocarbons in the saturated zone. Numerical solutions are obtained by approximating onedimensional flow as a series of completely mixed reactors and two-dimensional flow using an explicit finite difference solution corrected for numerical dispersion. One-dimensional model simulations indicate that biodegradation will be very rapid near the contaminant source when oxygen is present. When no oxygen is present at the source, biodegradation will be slow and limited by the transport of oxygen into the contaminant plume. Two-dimensional simulations indicate that horizontal and vertical mixing are the major sources of oxygen to the contaminant plume and control the biodegradation process. When adsorption of the hydrocarbon to the aquifer is significant, advective fluxes of oxygen into the plume and resulting biodegradation is also significant. Sensitivity analyses with the model suggest that for many aquifers the reaction between oxygen and hydrocarbon may be approximated as an instantaneous reaction since oxygen transport is rate limiting. Borden et al.¹⁴¹ employ these results to modify the U.S.G.S. Solute Transport Model²⁶³ to simulate oxygen-limited biodegradation of creosote wastes at a Superfund site. The model gave an adequate description of the observed oxygen and hydrocarbon distributions in the shallow aquifer at the site and was used to study various remedial actions, including no action and removal of the contaminant source.

Dawson et al.²⁶⁸ modify a petroleum reservoir code to simulate enhanced *in situ* biorestoration using the equations presented by Borden and Bedient.¹⁴⁰ Advective and dispersive transport is calculated using a finite element-modified MOC solution which allows a large time step and strongly advection-dominated flow. Because the rates of biodegradation can be very high relative to transport, a time-splitting scheme is employed where the microbial kinetic terms are solved separately using an implicit solution with a much smaller time step. This model is then employed to simulate enhanced *in situ* biorestoration by the injection of oxygen and production of contaminated water by a five-spot pattern. Simulations are performed for a variety of conditions including uniform and random permeabilities and variable adsorption.

F. Model Use and Limitations

The current technology for simulating subsurface biorestoration is still in its infancy. Some progress has been made in developing kinetic descriptions of the biodegradation process and combining these with available solute transport models. Unfortunately, little reliable field data have been available to rigorously test these models. Considerable uncertainty exists over the importance of simulating transport into biofilms or microcolonies. Also, the effects of variations in aquifer parameters on the efficiency of biorestoration are unknown. At present, the technology is not available to quantitatively predict the efficiency of enhanced biorestoration, but significant advances are being made in our ability to describe the process.

V. CONCLUSIONS

Of the available biological aquifer remediation techniques, the most effective demonstrated methods are enhancement of the native population and withdrawal and treatment by various wastewater treatment processes.²⁰⁹ Before any aquifer remediation technique can be implemented, a thorough understanding of the hydrogeology and contamination problems of the site must be obtained and used to design the treatment system.⁴ When successful, costs for *in situ* biorestoration are generally less than physical or chemical remediation techniques. *In situ* biorestoration compares favorably with other common remedial actions such as

excavation and withdrawal and treatment by carbon adsorption or air stripping.⁸⁷ Excavation is generally limited to surface soils above the water table and can be restricted by the physical construction on the site. Excavated soils must be transported to a secure landfill with the potential for liability from an accident during transport or a leak from the receiving landfill. The contaminated ground water must be withdrawn before air stripping and carbon adsorption. The ability to withdraw organic contaminants is a function of the solubility of contaminants and the permeability of the soil. Highly soluble organics in high-permeability soils can be effectively withdrawn. Compounds which are hydrophobic can be effectively treated with carbon adsorption, but because of their hydrophobicity are also more likely to be adsorbed to the soil and not removed by withdrawal systems. Carbon adsorption generates spent carbon that must be treated or sent to proper disposal facilities. Air stripping is effective for compounds with high volatilities, but not those with high boiling points or high solubilities. Air stripping simply transfers the contaminants to another phase of the environment unless expensive carbon adsorption or incineration is used to treat the off gases.

Addition of oxygen, nitrogen, phosphorus, and trace minerals stimulates the acclimated indigenous microbial population to aerobically degrade many subsurface contaminants. In situ biorestoration has been chiefly used to treat gasoline-contaminated aquifers, but also has been employed with ethylene glycol and solvents including acetone, tetrahydrofuran, methylene chloride, n-butanol, dimethyl aniline, and isopropanol. Biorestoration effectiveness will be affected by toxic levels of organics and heavy metals. In general, in situ bioreclamation has been effective in reducing the quantity of the contaminants but not in completely eliminating them. The treatment moves with the plume, allowing treatment of trapped or sorbed contaminants, or by using soil flushing or an infiltration gallery, in situ microbial treatment can reach areas that are not accessible by other techniques. Biorestoration has been used in a number of aquifers, but may be of limited usefulness in those with low permeabilities. Undesirable metabolic and inorganic nutrients may escape from the treatment zone and affect ground water or surface water quality. Alternative oxygen sources such as ozone, hydrogen peroxide, pure oxygen, and air flooding or soil venting may speed the removal of the organic contaminants, but their impact on the microbial population and the geochemistry of the site is not fully understood. Innovative processes such as treatment beds or land treatment can be used in some situations. In the presence of an acclimated microbial population, many aquifers will be anaerobic because the microorganisms will have depleted the dissolved oxygen. It will be possible to use anaerobic degradation to remove contaminants, although the technology for this treatment has not yet been developed. Reducing the interfacial tension between the hydrocarbon and ground water with surfactants, dispersants, or emulsifiers will mobilize the contaminants and may make them available for microbial degradation. Combinations of in situ biorestoration treatment with other chemical, physical, or biological treatment processes have been successfully utilized in aquifer remediation.

Treatment at the surface by biological wastewater processes is a proven technology. The biological processes include activated sludge, lagoons, waste stabilization ponds, fluidized bed reactors, trickling filters, rotating biological discs, and sequencing batch reactors. All of these processes are dependent upon extraction of the contaminated ground water from the subsurface. Combinations of conventional wastewater treatment processes and other water treatment processes have also been successful.

Alteration of the subsurface microbial community has a great deal of potential to allow degradation of recalcitrant compounds in the subsurface. The organisms are selected by enrichment culturing or genetic manipulation. However, introduction of non-native microorganisms may be limited by movement of the organisms through the subsurface, survival of the organisms, and accessibility of the organic contaminants. Addition of an acclimated population may be more successful when combined with wastewater treatment processes where the environment can be more closely regulated. Although the aquifer remedial actions that have used a microbial seed have not conclusively shown that the added organisms were

responsible for removal of the contaminant, the concentrations of the contaminants were reduced. Alteration of the environment to promote the activity of a particular component of the microbial community is another promising technology. Field tests and further research are currently underway for this technology. The environment is altered to promote the growth of organisms that co-oxidize halogenated aliphatics when supported on gaseous hydrocarbons such as methane, propane, or natural gas.

Techniques for simulating the subsurface biorestoration process are under development, but little reliable field data have been generated that can be applied to these models. Some of the major considerations in simulating transport and biodegradation of organic contaminants in the subsurface are poorly understood; these include the importance of transport of organics to the bacteria and the variability in aquifer parameters.

ACKNOWLEDGMENT

Although the research described in this article has been supported by the U.S. Environmental Protection Agency through Assistance Agreement No. CR-812808 to Rice University. it has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

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APPENDIX D

SUPPLEMENTARY MATERIAL FOR ONSITE BIOREMEDIATION

OF WOOD PRESERVING CONTAMINANTS IN SOILS

Dr. Ronald C. Sims, EPA-RSKERL, Ada, Oklahoma (Utah State University)

TECHNICAL	REPORT DATA	· · · · ·		
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TPA/600/2-88/055		PB89 1	09920/45	
A. TITLE AND SUSTITLE		5. REPORT DATE	1000	
CHARACTERIZATION AND LABORATORY SOIL TREATA	BILITY	September 1988		
STUDIES FOR CREOSOTE AND PENTACHLOROPHENOL	SLUDGES	6. PERFORMING OF	IGANIZATION CODE	
AND CONTAMINATED SUIL			CANIZATION REPORT NO	
G.D. McGinnis, H. Borazjani, L.K. McFarland and D.A. Strobel	, D.F. Pope			
9. PERFORMING ORGANIZATION NAME AND ADDRESS		10. PROGRAM ELEP	MENT NO.	
Mississippi forest froducts utilization Lab	oratory	CBWDI	LA	
Mississippi State. MS 39762		11. CONTRACT/GR	ANT NO.	
		CR-811	1498	
12. SPONSORING AGENCY NAME AND ADDRESS	·····	13. TYPE OF REPOR	T AND PERIOD COVERED	
Robert S. Kerr Environmental Research Lab.	- Ada, OK	Report	(10/87-06/88)	
U.S. Environmental Protection Agency		14. SPONSORING A	GENCY CODE	
Ada, OK 7/820		EPA/	/600/15	
Project Officer: John E. Matthews, FTS: 74	3-2333			
contained includes: 1) literature assessme treating chemicals; 2) sludge/soil charact and 3) degradatjon/toxicity data for wood Literature data indicated that creosote soil. Each sludge characterized contained of individual compounds varied among sludg traces of hepta/hexa dioxins and correspon PAH's with 2 rings generally exhibited	nt of soil tr erization dat treating chem /PCP waste co the PAH cons es. PCP slud ding furans.	eatability por a for 8 wood f icals in soils nstituents may tituents; rela ges contained	tential for wood treating sites; s from 4 sites. y be treatable in ative concentration PCP, OCCD, and	
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SECTION 4

EXPERIMENTAL SECTION

INTRODUCTION

This project was started on February 15, 1985 and consists of three phases: Phase I--site selection and characterization studies for defining selected soil and sludge characteristics at eight wood-treating sites; Phase II--laboratory treatability studies for determining rates of microbiological degradation or other transformation processes, soil transport properties of creosote and pentachlorophenol, and toxicity of the water-soluble fraction of waste soil mixtures; and Phase III--a field evaluation study at one of the eight wood-treating sites. The following is a summary of the experimental methods for the characterization phase and the laboratory treatability phase for four of the eight sites. A detailed methodology is presented in Appendix A.

SITE SELECTION CRITERIA

Eight wood-treating sites were selected in the southeastern United States, each having a different soil type. At each plant a site was selected approximately 1/2 to 1 acre in area which could be used for the field evaluation. The sites were selected using the following criteria:

- Site must have a source of sludges, preferably a separate source for PCP and creosote sludges.
- 2. Site should have low level exposure to PCP and creosote so that an acclimated bacteria population is available, but there should not be high levels of contamination within or below the treatment zone.

 There must be a method of collecting and disposing of run-off water from the site.

SITE, SOIL, AND SLUDGE CHARACTERIZATION

During the first visit to each plant site, one or more potential demonstration sites were selected and composite soil samples were collected. Soil samples were collected at 0-6 inches and 6-12 inches and subsequently analyzed for creosote and pentachlorophenol. Based on the chemical analysis, microbial population, and initial observations, one potential field evaluation site was selected at each plant location.

A second visit to each site was made in order to do a thorough site assessment as well as more complete chemical and microbiological characterization of the site soil. Soil samples were collected using a systematic sampling plan. The exact number of samples depended on the size of the area. The samples were then composited and analyzed.

A third visit was made to each site for soil evaluation. Soil profiles were examined at each site in freshly excavated pits and they were described and sampled using standard methods (Soil Survey Staff, 1951). Soil morphological descriptions included horizonation, Munsell color, texture, horizon boundaries, consistency, coarse fragments, root distribution, concretions and pedological features. Each horizon was sampled for laboratory analyses. Detailed analytical procedures used at each site are given in Appendix A.

LABORATORY TREATABILITY STUDIES

Transformation/Degradation Using a Standard Creosote/PCP Mixture: Experiment I

Phase II involved laboratory treatability studies for determining rates of degradation/transformation, soil transport properties of creosote and pentachlorophenol, and toxicity of the water-soluble fraction of waste soil mixtures. As a preliminary experiment to determine possible loading rates, sampling times, refine experimental techniques, and compare results in different soils using a common waste, an initial set of degradation/transformation experiments was conducted by applying, at 1% of the soil dry weight, a mixture of technical-grade pentachlorophenol and creosote at 200 and 2000 ppm, respectively (standard mixture) to a sample of each site's soil. Samples of each soil were taken at 0, 30, 60, and 90 days for chemical and microbiological analysis.

Transformation/Degradation of Site Specific Sludges: Experiment II

The second part of the laboratory degradation studies involved studying the kinetic rates using soil and sludges from the same site. The objective was to assess the feasibility of land treatment of the sludge present at a site in the soil at that site. Three sludge loading rates were tested, and the study was replicated three times. Soil samples were taken at 0, 30, 60, and 90 days for chemical and microbiological analysis.

SECTION 5

RESULTS AND DISCUSSION

SITE AND SOIL CHARACTERIZATION

The eight sites investigated represented very diverse soil, geologic, climatic, and environmental conditions. The sites ranged from near sea level in Gulfport, Mississippi and Wilmington, North Carolina to elevations above 1000 feet at Atlanta, Georgia. The study areas were located in six Major Land Resource Areas (MLRA) of the United States as shown in Table 14.

The sites encompassed several geomorphic landforms ranging from fluvial terraces to upland ridges. Soil parent materials varied from sandy Coastal Plain sediments and silty Peoria loess to granite gneiss residuum as shown in Table 15.

A brief discussion of the pertinent characteristics of each site is presented in the following paragraphs.

Grenada, MS--Moderately well-drained Loring soil comprises the site. Silt content exceeded 70% in the surface horizons and increased at deeper depths in the lower sola. Maximum clay content occurred in the Btxl horizon at depths of 16-26 inches. The fragipan horizons (Btxl, Btx2) had very low hydraulic conductivity and tended to perch water above the fragipan during the wetter winter and spring months. These layers greatly reduced downward leacheate movement. The surface horizon was strongly acid and pH levels increased with depth. Acidity (H) decreased in the deeper horizons as pH increases. Exchangeable Al levels reached a maximum level in the Btxl horizon at depths of 16-26 inches, comprising 30.7% of the cation exchange capacity. Mg and Ca

Site	MLRA					
Grenada, MS	134 - Southern MS Valley Silty Uplands					
Gulfport, MS	152A - Eastern Gulf Coast Flatwoods					
Wiggins, MS	133A - Southern Coastal Plain					
Columbus, MS	133A - Southern Coastal Plain					
Atlanta, GA	136 - Southern Piedmont					
Wilmington, NC	153A - Atlantic Coast Flatwoods					
Meridian, MS	133A - Southern Coastal Plain					
Chattanooga, TN	128 - Southern Appalachian Ridges and Valleys					

Table 14. Site location in Major Land Resource Areas.

Site	Sotl	Sand ^a	Silta	Clay ^a
Grenada, MS	Grenada silt loam	16.06	70.17	13.77
Gulfport, MS	Smithton	57.04	28.88	14.08
Wiggins, MS	McLaurin sandy loam	72.55	24.16	3.29
Columbus, MS	Latonia loamy sand	80.03	16.42	3.55
Atlanta, GA	Urban land		**	-*
Wilmington, NC	Urban land	91.5	6.0	2.5
Meridian, MS	Stough sandy loam	60.2	31.4	8.4
Chattanooga, TN	Urban land complex	13.01	46.77	40.22

Table 15. Overall field evaluation site soil composition.

^aThese samples were taken from the surface to a depth of 5 inches.

were the dominant metallic cations with levels increasing with depth. Electrical conductivity levels were low indicating no salt toxicity problems. Maximum total S content of 0.018% occurred in the surface horizon. Water holding capacity was high in the surface horizon. The clay fraction of the surface soil was dominated with kaolinite and mica (illite) with illite increasing in the subsoil and kaolinite decreasing.

Gulfport. MS--The site had 7 to 8 inches of mixed fill-soil overlying a poorly drained Smithton sandy loam soil. The site had slow runoff and subsoils that were moderately slow permeable subsoils. Maximum clay content (24.6%) occurred in the fill-soil capping and abruptly decreased to 3% in the subjacent, original surface horizon. Calcareous shells were common in the fill-soil, and were also mixed to the 7- to 12-inch layer. The calcareous materials were part of the fill-soil placed over the natural soil. The water table is near the surface during the wetter months. The added calcareous materials resulted in high levels of exchangeable Ca to depths of 38 inches which produced high base saturation levels and high pH levels (6.3 to 7.7). Low levels of Na were detected. Electrical conductivity values reflected the influence of the calcareous materials. Cation exchange capacity values were less than 6 me/100 g below depths of 12 inches. Total S levels were low with a maximum of 0.018% occurring in the A horizon at depths of 7 to 12 inches. The soil had relatively high available water holding capacity. Kaolinite was the dominant clay mineral in the surface horizon and subsoil. The fill-soil capping contained small amounts of smectite.

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Wiggins, MS--Deep, well-drained McLaurin sandy loam soils dominated this site. These soils had slow to medium runoff and moderate permeability. The soil was very strongly to strongly acid throughout the 60-inch solum. The soil was poly-genetic with two distinct clay maxima in the argillic horizon. Maximum clay content of 36.7% occurred at depths of 39 to 60 inches. The soil had low base saturation and cation exchange capacity, and electrical conductivity values reflected the low soluble salt content. The surface horizon had a high saturated conductivity value with variations in the subsoil due to the two clay maxima. The soil had low S contents with a maximum value occurring in the 39- to 60-inch horizon. The subsoil had low water holding capacity. Kaolinite was the dominant clay mineral in the surface and subsoil with lesser amounts of vermiculite-chlorite integrade.

Columbus, MS--A deep, well-drained sandy Latonia soil with moderately rapid permeable subsoil and slow runoff comprised the study area. The soil had loamy sand textures to a depth of 40 inches where gravelly sands occur. A maximum clay content of 7.5% occurred at depths of 17 to 25 inches. The soil was medium to strongly acid throughout the profile. Higher Ca levels were present in the upper horizons due to prolonged additions of leacheate from treated-wood products. The soil had elevated organic matter contents in the surface horizon from cultural additions which resulted in higher cation exchange capacity. Electrical conductivity values reflected the low soluble-salt content, with the highest levels in the surface horizon due to the added leacheate. Low contents of Mg, K, and Na were present throughout the profile. The highest S content of 0.095 occurred in the surface horizon. Kaolinite was the dominant clay mineral in the surface and subsoil horizons.

Atlanta, GA--The site had been truncated and the soil solum removed by cutting which exposed the subsoil C horizon and weathered saprolite parent material. The surface had accumulated organic carbon from additions of material in the pole yard. The partially weathered saprolite had high bulk density values and was firm in place, but tends to be loose when disturbed. The saprolite had low saturated hydraulic conductivity. The loose upper horizon had sandy loam textures. Clay content was less than 6% in the material sampled. The material was very strongly acid in the lower depths. Calcium is the dominant exchangeable cation. Cation exchange capacities are very low reflecting the low clay content. Kaolinite was the dominant clay mineral.

Wilmington, NC--The site was comprised of made land with 1 to 3 feet of sandy fill material over poorly drained sediments. The water table appeared to be affected by tidal fluctuations of the adjacent Cape Fear River. A water table at 21 inches and saturated sands below limited the depth of sampling. The soil had sand textures throughout the profile with a maximum clay content of 2.5% occurring in the surface horizon. The profile was moderately alkaline to neutral. Organic carbon had accumulated in the surface horizons from added materials. Calcium was the dominant exchangeable cation with low contents of other bases. Cation exchange capacity was essentially due to the added humus material, and value were less than 1 me/100 g at depths below 10 inches. Higher electrical conductivities occur in the upper layers analyzed due to added materials. The soil material had extremely high permeability with saturated hydraulic values of 34 inches/hr at depths below 10 inches. The material had low water-holding capacity below the surface. A complex mineral suite comprised the small clay fraction with kaolinite the dominant mineral.

Meridian, MS--Somewhat poorly drained Stough soils comprised the study area. These soils had slow runoff, moderately slow permeability, and were formed in thick beds of fluvial sediments. The soil had sandy loam upper horizons and loamy textured subsoils. Maximum clay content of 21.8% occurred at depths of 23 to 35 inches. Slightly firm, brittle horizons occurred at depths below 15 inches which tend to perch water during wet periods. The soil was strongly to very strongly acid throughout the profile. Acidity and calcium dominated the cation exchange complex. Kaolinite dominated the clay fraction of the surface and subsoil.

Chattanooga, TN--The site was located in a soil area mapped as urban land. The surface layer (0-4 inches) was a compacted mixture of limestone gravel and silty clay. The subsoil was a thick argillic horizon of silty clay and silty clay loam textures with slightly firm consistency. The surface horizon was mildly alkaline due to the limestone gravel additions, and the underlying profile was very strongly acid. The site was well-drained with no evidence of free water at depths of 90 inches. The soil had high bulk density and low saturated hydraulic conductivity. Available water-holding capacity was low. Maximum clay content of 49.2% occurred at depths of 38 to 44 inches. Exchangeable Ca, base saturation, and electrical conductivity were influenced by the limestone gravel in the surface horizon. Exchangeable aluminum comprised a significant proportion of the cation exchange complex in the subsurface horizons. The soil had a complex clay mineral suite dominated by kaolinite.

The general soil type and the amounts of sand, clay, and silt for each location are summarized in Table 15.

Chemical Analysis of Wood-Treating Chemicals in the Soil

One of the main concerns in selecting a field evaluation site for this study was levels of background chemicals in the soil. Chemical analyses of the amount of pentachlorophenol, creosote, and octachlorodibenzo-p-dioxin at various depths are summarized in Tables 16-18. Grenada, Gulfport, and Columbus had no detectable levels of pentachlorophenol below 10 inches. The Wiggins site had pentachlorophenol down to 20 inches, while the other sites had detectable levels down to 60 inches or to ground water. The detection limit for pentachlorophenol in soil was 27 ppb. Soil from Grenada, Gulfport, Atlanta, Meridian, Wiggins, and Chattanooga had no detectable levels of PAH's below 10 inches while those from Columbus and Wilmington had PAH's down to 20 inches or deeper. Octachlorodibenzo-p-dioxin levels at the soil surface (0-6 inches) varied from none detected to 2.38 ppm (Table 18). The soil and sludge detection limits for the individual PAH's, OCDD, and for PCP are given in Appendix A.

Microbial plate counts for soils at each site are presented in Table 19. Counts of bacteria were done on potato dextrose agar (PDA), alone, or with various additives. This data provides an approximate number of total soil bacteria and fungi, as well as the number of soil bacteria that can tolerate or utilize creosote or pentachlorophenol.

Depth (inches)	Grenada	Gulfport	Wiggins Pentachlo	Columbus prophenol c	Atlanta concentration	Wilmington n (ppm in so	Meridian il)	Chattanooga
0-10	NDa	0.112	0.389	ND	20,64 ^b	1.418	0,129 ^b	0,288 ^b
10-20	ND	ND	0.017	ND	0.088	0.218	0.090	0.099
20-30	ND	ND	ND	ND	0.130	0.209 ^C	0.096	0.090
30-40	ND	ND	ND	ND	0.147	(ras 645	0.104	0.074
40-50	ND	ND	ND	ND	0.319		0.053	0.057
50-60	ND	ND	ND	ND				

Table 16. Soil concentration of PCP at the proposed field evaluation sites.

 $^{a}ND = Not Detected.$

^bThis value is the average of 4 values, two samples were taken at 0-6 inches, and two were taken from 6-10 inches.

^CThe maximum depth that soil could be collected at this site was 20 to 23 inches due to the high levels of ground water.

Depth (inches)	Grenada	Gulfport	Wiggins Total	Columbus polycyclic	Atlanta aromatics	Wilmington in soil ^a (ppm	Meridian)	Chattanooga
0-10	NDD	1.78	0.33	195.9 C	110.81 ^d	193.3	ND	121.76 ^g
10-20	ND	ND	ND	27.45 ^e	ND	40.55	ND	ND
20-30	ND	ND	ND	ND ^f	ND	43.94 [†]	ND	ND
30-40	ND	ND	ND	ND	ND		ND	ND
40-50	ND	ND	ND	ND	ND		ND	. ND
50-60	ND	ND	ND	ND	ND	5m 60	ND	100 000

Table 17. Soil concentration of PAH's at the proposed field evaluation sites.

^aThe total concentration of 16 polycyclic aromatic hydrocarbons (naphthalene, 2-methylnaphthalene, 1-methylnaphthalene, biphenyl, acenaphthylene, acenaphthene, dibenzofuran, fluorene,

phenanthrene, anthracene, carbazole, fluoranthene, pyrene, 1,2-benzanthracene. chrysene.

benzo(a)pyrene, benzo(ghi)perylene. ^DNormal 16 PAH compounds were detectable in the soil sample.

CSample taken between 0 to 6 inches. dSample taken between 6 to 16 inches.

eSample taken between 16 to 26 inches.

^fAnalysis done between 20 to 23 inches (ground water was at 23 inches and below). ^gAverage value of 4 samples (2 samples taken from 0 to 6 inches and 2 samples taken from 6 to 10 inches).

^{END} = Not Detected.

•	Octachlorodibenzo-p-dioxin (ppm) ^a
Grenada	0.12 + 0.22
Gulfport	0.37 ± 0.24
Wiggins	0.077 ∓ 0.19
Columbus	0.034 ± 0.22
Atlanta	2.13 ± 0.34
Wilmington	NDD
Meridian	ND
Chattanooga	0.36 <u>+</u> 0.57

Table 18. Soil concentration of octachlorodibenzo-p-dioxin at the proposed land treatment sites (0 to 6 inches).

^aThese samples represent soil at 0 to 6 inches and are the average of a minimum of three replicates <u>+</u> standard deviation.

 $b_{ND} = Not Detected.$

Site		Types of media (counts/gram)						
	Soil Depth	PDA	PDAA	PDA + creosote	PDA + penta- chlorophenol	PDA + creosote & pentachlorophenol		
Atlanta	0-6*	900,000	60,000	700,000	450,000	450,000		
Chattanooga	0-6*	473,000	23,000	203,000	30,000	·6,000		
Columbus	0-6*	290,000	120,000	220,000	20,000	10,000		
Grenada	0-6"	1,000,000	180,000	600,000	110,000	125,000		
Gulfport	0-6*	1.800.000	100,000	1.000.000	90,000	100,000		
Meridian	0-6"	1,683,000	141,000	1,600,000	466,000	250,000		
Wiggins	0-6*	1,200,000	80,000	500,000	000,03	80,000		
Wilmington	0-6"	763.000	40,000	523,000	166,000	66,000		

Table 19. Microbial plate counts at proposed field evaluation sites.^a

^aEach figure represents an average of three replications. The values were obtained by adding 0.1 mg of soil diluted with 9.9 mg of sterile soil to each plate.

Table 20. Nitrogen and phosphorous at the eight selected sites.^a

	Grenada	Gulfport	Viggins	Columbus	Atlanta - ppm	Wi Imington	Meridian	Chattanooga
Total Nitrogen	1709	1999	1150	1598	1501	1231	2990	2000
Total Phosphorous	310	292	255	338	254	597	315	237

^aBased on dry weight.
The nitrogen and phosphorous contents for the soil at each site are given in Table 20.

Sludge Characterization

Each plant site had different types of sludges. Six of the plants had open lagoons of creosote and/or pentachlorophenol; one site had three lagoons which were segregated into pentachlorophenol, pentachlorophenol in a heavy oil, and creosote; two other plants had no lagoons but had areas of dried sludge and contaminated soil (see Table 21).

The water content, total organic and inorganic materials, pH, and total organic carbon are summarized in Table 22. Water contents of these samples varied from 26.6 to 74.58%. The total organic material ranged from 8.96 to 68.0%. The pH varied from 3.00 to 7.20. The more acidic sites contained large amounts of PCP. The total organic carbon varied from 4.02 to 49.79%. The wide variation in inorganic solids is not surprising since these sludges are stored in large open lagoons. The pH is related to the concentration of PCP in sludge and probably is also affected by the soil pH. The high levels of organic materials are mainly the heavy oils used to dissolve PCP for treating wood and the aliphatic fraction found in creosote.

Total phenolics, oil and grease, nitrogen phosphorus, and chloride content of the sludges are summarized in Table 23. Concentrations of pentachlorophenol and polycyclic aromatic hydrocarbons in the sludges are given in Table 24. A more detailed list of the individual concentration of PAH's in each sludge is given in Table 25.

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Site location	Size & age of plant	Preservative used	Number & type of lagoons
Grenada, MS	100 acres 78 years old	Both penta- chloropenol and creosote	Lagoons are closed; contaminated soil and sludge are present
Gulfport, MS	100 acres 80 years old	Both penta- chlorophenol (65%) and creosote (35%)	Large lagoon of mixed preservatives and contaminated soil
Wiggins, MS	100 acres 15 years old	Both penta- chlorophenol (60%) and creosote (40%)	Individual lagoons of 1) pentachlorophenol, 2) pentachlorophenol in heavy oil, and 3) creosote
Columbus, MS		Creosote (100%)	Contaminated soil and lagoon
Atlanta, GA	15 acres 63 years old	Both penta- chloropheno] (80%) and creosote (20%)	Contaminated soil and lagoon
Wilmington, NC ^a		Both penta- chlorophenol and creosote	Lagoons are closed but contaminated soil is available
Meridian, MS	125 acres 61 years old	Both penta- chlorophenol (25%) and creosote (75%)	Large lagoon and con- taminated soil available
Chattanooga, TN	76 acres 62 years old	Creosote (100%)	Enclosed lagoons and contaminated soil

Table 21. Characteristics of the eight sites used in this study.

^aThis site has been an active land farming site for 1 1/2 years.

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	Water content (%)	Total organic materials (%)	Inorganic solids (%)	рН	Total organic carbon (%)
Grenada	74.58	24.31	1.11	6.30	7.37
Gulfport	30.62	68.00	1.38	4.80	22.50
Wiggins #1	36.07	40.58	23.35	3.00	37.85
Wiggins #2 ^C Wiggins #3 ^d Columbus	31.56 36.52 34.44 59.10	26.02 27.80 61.11 23.75	42.42 35.68 4.45 7.14	3.50 5.70 5.90	49.45 36.03 49.79 25.33
Wilmington	26.60	8.96	64.44	7.20	4.02
Meridian	48.27	50.00	1.73	4.00	31.96
Chattanooga	67.35	15.74	16.91	7.10	14.61

Table 22. Composition of the sludges.^a

Table 23. Chemical composition of the sludges.^a

Site	Total phenolics (%)	0il and grease (%)	Nitrogen (ppm)	Phosphorous (ppm)	Inorganic chloride content (ppm)
Grenada	.0041	9.74	7562	236	267
Gulfport	.0097	44.03	2949	506	440
Wiggins #10	.0045	15.86	1119	446	361
Wiggins #2 ^C	.0130	22.57	1141	477	753
Wiggins #3 ^d	.0171	17.90	640	261	825
Columbus	.0224	44.60	2951	270	49
Atlanta	.0120	14,17	1730	316	278
Wilmington	.0007	0.44	1283	435	1138
Meridian	.0114	35.34	3621	213	220
Chattanooga	.0003	3.68	2090	417	28

^aAll data reported on the starting weight of sludge. ^bLagoon contains mainly pentachlorophenol. ^cLagoon contains mainly pentachlorophenol in a heavy oil. ^dLagoon contains mainly creosote.

Site	Pentachlorophenol (ppm)	Polycyclic aromatic hydrocarbons ^D (ppm)	Octachloro- dibenzo-p- dioxin (ppm)
Grenada	6,699	96,078	23
Gulfport	5,656	101.023	215
Wiggins #1	29.022	20,463	114
Wiggins #2	30,060	47,075	125
Wiggins #3	1,893	114,127	21
Columbus	NDC	475,372	ND
Atlanta	51,974	119,546	160
Wilmington	NO	10,007	ND
Meridian	13,891	119,124	160
Chattanooga	ND	72,346	ND

Table 24. Concentration of PCP and total PAH's in each sludge sample.^a

^aThese values are the means of two replicates and are determined on a dry basis. All were determined by capillary column gas chromatography.

^bTotal of the 17 major polycyclic aromatic hydrocarbons found in creosote.

^CND = Not detected. See Appendix A for detection limits.

	N	2Ma	1Hn .	81	Ac	Ace	D1	FI	Ph	An	Ca	Flu	Py	1,28	Ch	Bz	Øzg
Grenada	67000	24150	1 3250	5850	5250	21500	17000	18000	43000	15000	3450	27000	19500	3250	5850	3600	5050
Gulfport	1 3500	14000	7450	3000	2635	10150	9600	10250	30000	7200	2100	17000	12500	2050	3650	1050	ND ^b
Wiggins #1	3400	2450	1400	535	215	1550	1300	1750	5000	2550	570	2150	1500	185	495	75	ND
Wiggins #2	10200	7450	4000	1900	1050	5550	605 0	7450	21000	8150	2650	11500	7500	1300	2400	355	NO
Wiggins #3	17500	12000	6350	3500	2000	13000	11500	14000	34000	14500	4250	22500	19000	3850	6000	580	ND
Columbus	70500	29500	16500	10500	7650	31000	32500	34000	53000	23000	12500	49500	38000	12500	17000	3500	6850
Atlanta	39400	23000	11500	6600	2800	16500	16000	18000	45000	24500	9550	23000	15500	3400	5800	1100	8050
Wilmington	350	330	185	ND	ND	400	425	585	1550	1525	190	840	430	150	150	ND	ND
Her 1d tan	16500	5350	2700	1650	1800	5150	6850	7350	29500	6550	2050	20000	11700	2200	4800	1350	550
Chattanooga	1200	815	585	445	ND	1230	1150	1415	5400	2200	870	3550	2100	200	200	ND	ND
N = Naphtha 2Mn = 2-Methy 1Mn = 1-Methy B1 = Bipheny Ac = Acenaph	alene ylnaphtha ylnaphtha yl yl yl	lene lene	D1 = F1 = Ph = An = Ca =	Dibenzof Fluorene Phenanth Anthrace Carbazol	uran rene ne	Py = 1,28 = Ch = 8z = Bzg =	Pyrene 1,2-Benz Chrysend Benzo(a) Benzo(a)	canthrac P pyrene	ene								

Pentachlorophenol

Table 25. Concentration of creosote and PCP in sludges from the selected sites^a (μ g/g dry weight).

^aThese values were obtained by GC/MS.

Flu = Fluoranthene

^bNB = Not detected.

Ace = Acenaphthene

The results in Table 24 are obtained by capillary column gas chromatography while the results in Table 25 are obtained using GC/MS. Gas chromatography/mass spectrometry was also used to identify some of the minor constituents in the sludges. The results are summarized in Table 26.

The trace metal content of the sludges are summarized in Table 27. The most common metals found at most wood-treating plants are mixtures of copper chromium and arsenic salts. None of the sludges had high levels of chromium and arsenic. None of the sites had used fire retardant treatments $(ZnCl_2)$.

LABORATORY TRANSFORMATION/DEGRADATION STUDIES

Transformation/Degradation Using a Standard Creosote/PCP Mixture: Experiment I

The results of Experiment I are shown in Figures 4 and 5 for the microbiological data, and Tables 28 through 36 for transformation/ degradation rates.

Gulfport soil was able to transform all the PAH's analyzed, with only two (pyrene and benzo-a-pyrene) having relatively slow breakdown rates. Columbus soil was able to transform all PAH's but anthracene, though at somewhat slower rates than Gulfport for most PAH's. Gulfport and Columbus developed higher levels of acclimated organisms than the other sites, possibly accounting for the better transformation. Soil from the other sites transformed most of the lower molecular weight PAH's readily. Many of the higher molecular weight PAH's (fluoranthene, pyrene, 1,2-benzanthracene, chrysene, and benzo-a-pyrene) tended to transform slowly if at all. Pyrene and fluoranthene were perhaps the most recalcitrant.

	Possible compounds	Site location and number of isomers									
Molecular weight		6r	Gp	W1#1	W1#2	311/3	Co	At	Vin	Hr	Ch
156	dimethylnaphthalene, ethylnaphthalene	2	3	2	3	2	1	3			
168	methyldiphenyl, methylacenaphthene, diphenylmethane						1				**
170	trimethylnaphthalene	**	1	2							**
182	dimethylbiphenyl, ethylbiphenyl, methyldibenzofuran, dimethylacenaphthene		••		*•	2	2	1			
184	dibenzoth lopene, tetramethy lnaphthalene	1					1	1		1	
192	methylphenanthrene, methylanthracene, phenylindene	3	3		3	2	3	3	••	3	
204	phenylnaphthalene, vinylphenanthrene, vinylanthracene					1	1			1	••
216	<pre>methylfluoranthene, methylpyrene, benzofluorene</pre>	2	2		1	1	2	2		2	
218	benzonaphthofuran	1	1	**	1		1	1		1	
226	benzo(gh1)fluoranthene, cyclopenta(cd) pyrene					••		1		1	
252	benzo(k)fluoranthene, perylene, benzo(e) pyrene, benzo(abj)fluoranthene, and others	1	1				2	2			
230	tetrachlorophenol			1	1	1		1			

Table 26. Minor components present in sludge.

At = Atlanta, GA Gp = Gulfport, MS

Ch = Chattanooga, TN Hr = Heridian, HS

Co = Columbus, NS V1 = Wiggins, NS

Gr = Grenada, HS im = Wilmington, NC

Table 27. Concentration of metals in each sludge sample.

Site	Arsen1c µg/g	Ant Imony µg/g	Bartum µg/g	Berylium µg/g	<u>Cadmtum</u> µg/g	<u>Chromtum</u> µg/g	<u>Cobalt</u> µg/g	<u>Lead</u> µg/g	Mercury µg/g	Nickel µg/g	Selentum µg/g	Vanad1um }⊥g/g
Atlanta, 6A	<.715	<1.50	<0.10	<0.100	<0.200	35.14	0.38	<2.00	0.012	5.82	<0.500	1.78
Chattanooga, TN	<0.500	<1.50	3.32	1.792	<0.200	26.48	<0.30	<2.00	800.0	27.26	0.612	3.64
Columbus, MS	<0.500	<1.50	<0.10	<0.100	0.251	13.11	<0.30	12.43	<0.001	14.97	<0.500	<0.50
Grenada, MS	<0.500	<1.50	<0.10	<0.100	<0.200	5.85	0.35	<2.00	<0.001	7.19	<0.500	<0.50
Gulfport, MS	0.647	<1.50	1.35	0.281	0.143	6.64	<0.30	<2.00	0.003	1.05	<0.500	4.87
Heridian, HS	<0.500	<1.50	<0.10	<0.100	0.160	1.16	<0.30	8.17	0.002	0.30	0.529	1,51
Wilmington, NC	2.491	<1.560	1.83	0.823	<0.200	20.60	<0.30	<2.00	0.003	7.66	<0.500	6.79
Wiggins, MS #1	0.562	<1.50	4.05	0.521	<0.200	6.65	5.84	<2.00	<0.001	4.85	<0.500	1.48
Wiggins, MS #2	<0.508	<1.50	0.14	0.493	<0.200	8.39	0.85	<2.00	<0.001	10.91	<0.500	<0.50
Viggins, MS /3	<0.500	<1.50	<0.10	0.384	<0.200	25.34	2.32	<2.00	<0.001	17.00	<0,500	2.02

(a) Concentration of metals was determined by digestion method (302E, APHA Standard HTHDS, 16th Edition, pp. 148-149), and Inductively Coupled argon Plasma spectroscopy (ICP).

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Figure 4. Bacteria counts from all eight sites at 1% and 0% loading rates after the final addition of the standard mixture.

^aTotal bacteria counts on PDA media.



Figure 5. Acclimated bacteria counts from all eight sites at 1% and 0% loading rates after the final addition of the standard mixture.

^aBacteria acclimated to both PCP and creosote.

Compounds	Loading Dry Wt. (%)	K (day-1)	T 1/2 (days)
Naphthalene 2-Methylnaphthalene 1-Methylnaphthalene Biphenyl Acenaphthylene Acenaphthene Dibenzofuran Fluorene Phenanthrene Anthracene Carbazole Fluoranthene Pyrene 1,2 Benzanthracene	1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0	-0.193 -0.190 -0.183 -0.179 -0.170 -0.200 -0.192 -0.192 -0.203 -0.179 -0.184 -0.024 -0.001 -0.194	4 4 4 4 3 4 4 3 4 4 29 1155 4
Chrysene Benzo-a-pyrene Benzo-ghi-perylene	1.0 1.0 1.0	-0.189 -0.002 -0.174	4 365 4

Table 28. Kinetic data for PAH degradation/transformation in Gulfport soils.

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Compounds	Loading Dry Wt. (%)	K (day-1)	T 1/2 (days)
Naphthalene 2-Methylnaphthalene 1-Methylnaphthalene Biphenyl Acenaphthylene Acenaphthene Dibenzofuran Fluorene Phenanthrene Anthracene Carbazole Fluoranthene Pyrene 1,2 Benzanthracene Chrysene Benzo-a-pyrene Benzo-ghi-perylene	1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0	-0.332 -0.328 -0.316 -0.025 -0.042 -0.014 -0.063 -0.039 -0.061 NT ^a -0.009 -0.012 -0.012 -0.015 -0.014 -0.009 -0.286	2 2 28 16 50 11 18 11 NT 81 59 58 47 49 82 2

Table 29.	Kinetic data for PAH degradation/transformation i	n
	Columbus soils.	

^aNT = no transformation observed.

Compounds	Loading Dry Wt. (%)	K (day-1)	T 1/2 (days)
Naphthalene	1.0	-0,191	4
2-Methylnaphthalene	1.0	-0.189	4
1-Methylnaphthalene	1.0	-0.181	4
Bipheny1	1.0	-0.178	4
Acenaphthylene	1.0	-0.235	3
Acenaphthene	1.0	-0.202	3
Dibenzofuran	1.0	-0.255	3
Fluorene	1.0	-0.258	3
Phenanthrene	1.0	-0.267	3
Anthracene	1.0	-0.241	3
Carbazole	1.0	-0.056	12
Fluoranthene	1.0	NTa	NT
Pyrene	1.0	-0.002	289
1,2 Benzanthracene	1.0	NT	NT
Chrysene	1.0	NT	NT
Benzo-a-pyrene	1.0	-0.006	116
Benzo-ghi-perylene	1.0	-0.166	4

Table 30. Kinetic data for PAH degradation/transformation in Grenada soils.

 a NT = no transformation observed.

Compounds	Loading Dry Wt. (%)	K (day-1)	T 1/2 (days)
Naphthalene 2-Methylnaphthalene 1-Methylnaphthalene Biphenyl Acenaphthylene Acenaphthene Dibenzofuran Fluorene Phenanthrene Anthracene Carbazole Fluoranthene Pyrene 1,2 Benzanthracene Chrysene Benzo-a-pyrene Benzo-ghi-perylene	1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0	-0.132 -0.193 -0.187 -0.181 -0.009 -0.010 -0.013 -0.015 -0.011 -0.008 NT ^A -0.001 NT -0.002 NT NT -0.008	5 4 4 77 72 52 47 63 91 NT 990 NT 3655 NT NT 84

Table 31. Kinetic data for PAH degradation/transformation in Chattanooga soils.

^aNT = no transformation observed.

Compounds	Loading Dry Wt. (%)	K (day-1)	T 1/2 (days)
Naphthalene	1.0	-0.193	4
2-Methylnaphthalene	1.0	-0.196	4
1-Methylnaphthalene	1.0	-0.188	4
Biphenyl	1.0	-0.185	4
Acenaphthylene	1.0	-0.186	4
Acenaphthene	1.0	-0.013	52
Dibenzofuran	1.0	-0.137	5
Fluorene	1.0	-0.009	79
Phenanthrene	1.0	-0.010	68
Anthracene	1.0	NTª	NT
Carbazole	1.0	-0.180	4
Fluoranthene	1.0	-0.004	189
Pyrene	1.0	-0.001	1085
1,2 Benzanthracene	1.0	NT	NT
Chrysene	1.0	-0.004	158
Benzo-a-pyrene	1.0	-0.180	4
Benzo-ghi-pervlene	1.0	-0.114	6

Table 32. Kinetic data for PAH degradation/transformation in Wilmington soils.

^aNT = no transformation observed.

Compounds	Loading Dry Wt.	K (day-1)	T 1/2 (days)
	(%)		
Naphthalene 2-Methylnaphthalene 1-Methylnaphthalene Biphenyl Acenaphthylene Acenaphthene Dibenzofuran Fluorene Phenanthrene Anthracene	1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0	-0.185 -0.186 -0.179 -0.186 -0.174 -0.255 -0.262 -0.258 -0.217 ND ^a	4 4 4 3 3 3 3 ND 4
Carbazole Fluoranthene Pyrene 1,2 Benzanthracene Chrysene Benzo-a-pyrene Benzo-ghi-perylene	1.0 1.0 1.0 1.0 1.0 1.0	NT NT NT NT NT NT ND	NT NT NT NT NT ND

Table 33. Kinetic data for PAH degradation/transformation in Meridian soils.

 a ND = not detected.

bNT ***** no transformation observed.

Compounds	Loading Dry Wt. (%)	K (day-1)	T 1/2 (days)
Naphthalene	1.0	-0.181	4
2-Methylnaphthalene	1.0	-0.181	4
1-Methylnaphthalene	1.0	-0.178	4
Bipheny 1	1.0	-0.171	4
Acenaphthylene	1.0	-0.164	4
Acenaphthene	1.0	-0.020	35
Dibenzofuran	1.0	-0.193	4
Fluorene	1.0	-0.254	3
Phenanthrene	1.0	-0.024	29
Anthracene	1.0	-0.175	4
Carbazole	1.0	-0.174	4
Fluoranthene	1.0	NTa	NT
Pyrene	1.0	NT	NT
1.2 Benzanthracene	1.0	NT	NT
Chrysene	1.0	NT	NT
Benzo-a-pyrene	1.0	NT	NT
Benzo-ghi-perylene	1.0	-0.167	4

Table 34. Kinetic data for PAH degradation/transformation in Atlanta soils.

^aNT = no transformation observed.

Compounds	Loading Dry Wt. (%)	K (day-1)	T 1/2 (days)
Naphthalene 2-Methylnaphthalene 1-Methylnaphthalene Biphenyl Acenaphthylene Acenaphthene Dibenzofuran Fluorene Phenanthrene Anthracene Carbazole Fluoranthene Pyrene 1,2 Benzanthracene Chrysene Benzo-a-pyrene Benzo-ghi-perylene	1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0	-0.318 -0.313 -0.301 -0.294 -0.299 -0.338 -0.319 -0.329 -0.342 -0.309 -0.305 NT ^a NT -0.006 NT -0.302 -0.284	2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2

Table 35.	Kinetic Wiggins	data soils	for	PAH	degradation/transformation	in
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 a NT = no transformation observed.

Site	Loading Dry Wt. (%)	K (day-1)	T 1/2 (days)	
iulfport	1.0	-0.0107	64	
irenada	1.0	-0.0024	289	
olumbus	1.0	NT ^a	NT	
tlanta	1.0	NT	NT	
iggins	1.0	NT	NT	
hattanooga	1.0	-0.0027	259	
lilmington	1.0	-0.0022	320	
leridian	1.0	-0.0009	815	

Table 36. Kinetic data for PCP degradation/transformation in site soils.

^aNT = no transformation observed.

PCP transformation occurred in Gulfport, Grenada, Chattanooga, Wilmington, and Meridian soils. PCP half life was 64 days in Gulfport soil, but well over 100 days for the other soils. Columbus, Atlanta, and Wiggins soil exhibited no transformation of PCP.

The results of this preliminary experiment indicate that all of the Compounds studied can be transformed in soils at practically useful rates under the appropriate conditions. Microorganism counts of the type used in this experiment do not appear to be extremely accurate indicators of potential breakdown rates for particular compounds. However, there is some tendency for soils with higher populations of acclimated microorganisms to transform more of the different PAH's in creosote sludge at practically useful rates. This might be due to larger numbers of particular microorganisms or to a more diverse array of microbial species.

Since some of the soils exhibited no breakdown of particular PAH's, it would be desirable to test a range of loadings in subsequent experiments to see if lower loading rates might allow enhanced transformation in these soils.

Transformation/Degradation of Site Specific Sludges: Experiment II

The results of Experiment II are shown in Tables 37 through 42 for transformation/degradation kinetic data and Table 43 for microbiological data.

The total PAH breakdown was similar in soils from all four sites for similar loading concentrations. The individual PAH's can be divided into three groups; those with half lives of ten days or less, those with half lives of one hundred days or less, and those with half

				95%	95% Confidence Interval			
				Lower Limit		Upper Limit		
Compounds	Loading Dry Wt. (%)	K (day-1)	T 1/2 (days)	(day-1)	T 1/2 (days)	K (day-1)	T 1/2 (days)	
Naphthalene	0.33	-0.535	1	-0.573	1	-0.498	1	
2-Methylnaphthalene	0.33	-0.536	. 1	-0.551	1	-0.521	1	
1-Methylnaphthalene	0.33	-0.531	1	-0.537	1	-0.524	1	
Bipheny1	0.33	-0.513	1	-0.520	1	-0.507	1	
Acenaphthylene	0.33	-0.508	1	-0.517	1	-0.498	1	
Acenaphthene	0.33	-0.187	4	-0.288	2	-0.086	8	
Dibenzofuran	0.33	-0.202	3	-0.242	3	-0.162	4	
Fluorene	0.33	-0.204	3	-0.241	3	-0.167	4	
Phenanthrene	0.33	-0.039	18	-0.064	11	-0.014	50	
Anthracene	0.33	-0.015	46	-0.020	35	-0.010	68	
Carbazole	0.33	-0.020	35	-0.024	30	-0.016	43	
Fluoranthene	0.33	-0.013	53	-0.024	29	-0.003	248	
Pyrene	0.33	-0.003	231	-0.007	100	NTa	NT	
1.2 Benzanthracene	0.33	-0.002	347	-0.006	122	NT	NT	
Chrysene	0.33	-0.007	102	-0.011	61	-0.002	301	
Benzo-a-pyrene	0.33	NT.	NT	NT	NT	NT	NT	
Benzo-ghi-perylene	0.33	NDP	ND	ND	ND	ND	ND	

Table 37. Kinetic data for PAH degradation/transformation in Columbus soils.

 $a_{\rm NT}$ = no transformation observed.

^bND = not detected.

				95% Confidence Interval			
			T 1/2 (days)	Lower	Limit	Upper Limit	
Compounds	Loading Dry Wt. (%)	K (day-1)		K (day-1)	T 1/2 (days)	K (day-1)	T 1/2 (days)
Naphthalene 2-Methylnaphthalene 1-Methylnaphthalene Biphenyl Acenaphthylene Acenaphthene Dibenzofuran Fluorene Phenanthrene Anthracene Carbazole Fluoranthene Pyrene 1,2 Benzanthracene Chrysene Benzo-a-pyrene Benzo-ghi-perylene	1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0	-0.049 -0.096 -0.207 -0.149 -0.074 -0.028 -0.325 -0.022 -0.027 NT -0.009 -0.002 -0.002 -0.002 -0.001 -0.002 NT NT	14 7 3 5 9 25 2 31 25 NT 75 289 433 578 365 NT NT	-0.072 -0.169 -0.252 -0.228 -0.152 -0.041 -0.040 -0.031 -0.041 NT -0.015 -0.004 -0.004 -0.004 -0.004 NT NT	10 4 3 5 17 17 22 17 NT 48 165 187 173 173 173 NT NT	-0.025 -0.023 -0.162 -0.070 NT -0.014 -0.025 -0.013 -0.014 NT -0.004 -0.001 NT NT NT NT NT	28 29 4 10 NT 50 28 52 50 NT 169 1155 NT NT NT NT

Table 37. Kinetic data for PAH degradation/transformation in Columbus soils. (continued)

			K T 1/2 ay-1) (days)	95%	95% Confidence Interval				
				Lower	<u>Limit</u>	Upper Limit			
Compounds	Loading Dry Wt. (%)	K (day-1)		K (day-1)	T 1/2 (days)	K (day-1)	T 172 (days)		
Naphthalene	3.0	-0.050	14	-0.066	11	-0.033	21		
2-Methylnaphthalene	3.0	-0.029	24	-0.037	19	-0.021	33		
1-Methylnaphthalene	3.0	-0.018	39	-0.024	28	-0.011	61		
Biphenyl	3.0	-0.012	57	-0.023	30	-0.001	578		
Acenaphthylene	3.0	-0.006	112	-0.008	89	-0.005	147		
Acenaphthene	3.0	-0.006	124	-0.007	96	-0.004	169		
Dibenzofuran	3.0	-0.005	147	-0.007	99	-0.002	301		
Fluorene	3.0	-0.003	224	-0.004	169	-0.002	347		
Phenanthrene	3.0	-0.001	578	-0.004	173	NT	NT		
Anthracene	3.0	-0.004	173	-0.007	96	-0.001	866		
Carbazole	3.0	-0.008	90	-0.011	62	-0.004	169		
Fluoranthene	3.0	-0.007	107	-0.010	67	-0.003	267		
Pyrene	3.0	-0.007	99	-0.011	62	-0.003	248		
1.2 Benzanthracene	3.0	-0.002	315	-0.009	82	NT	NT		
Chrysene	3.0	-0.007	98	-0.015	47	NT	NT		
Benzo-a-pyrene	3.0	NT	NT	NT	NT	NT	NT		
Benzo-ghi-perylene	3.0	-0.004	158	-0.011	61	NT	NT		

Table 37. Kinetic data for PAH degradation/transformation in Columbus soils. (continued)

				95%	95% Confidence Interval			
				Lower	Limit	Upper L	imit	
Compounds	Loading Dry Wt. (%)	K (day-1)	T 1/2 (days)	K (day-1)	T 1/2 (days)	K (day-1)	[1/2 (days)	
Naphthalene	0.33	-0.531	1	-0.560	1	-0.502	1	
2-Methylnaphthalene	0.33	-0.529	1	-0.549	1	-0.508	1	
1-Methylnaphthalene	0.33	-0.498	1	-0.519	1	-0.476	1	
Bipheny1	0.33	-0.484	1	-0.486	1	-0.482	1	
Acenaphthylene	0.33	-0.154	4	-0.279	2	-0.030	23	
Acenaphthene	0.33	-0.163	4	-0.251	3	-0.075	9	
Dibenzofuran	0.33	-0.160	4	-0.243	3	-0.077	9	
Fluorene	0.33	-0.161	4	-0.257	3	-0.065	11	
Phenanthrene	0.33	-0.126	5	-0.215	3	-0.038	18	
Anthracene	0.33	-0.067	10	-0.142	5	NTª	NT	
Carbazole	0.33	-0.255	3	-0.378	2	-0.132	5	
Fluoranthene	0.33	-0.011	65	-0.014	51	-0.008	. 91	
Pyrene	0.33	-0.010	68	-0.013	53	-0.007	95	
1,2 Benzanthracene	0.33	-0.001	3466	-0.004	169	NT	NT	
Chrysene	0.33	-0.004	173	-0.007	95	-0.001	866	
Benzo-a-pyrene	0.33	-0.001	3466	-0.002	433	NT	NT	
Benzo-ghi-perylene	0.33	-0.001	770	-0.006	126	NT	NT	

Table 38. Kinetic data for PAH degradation/transformation in Grenada soils.

 $a_{NT} = no$ transformation observed.

^bND = not detected.

			T 1/2 -1) (days)	95% Confidence Interval				
				Lower Limit		Upper Limit		
Compounds	Loading Dry Wt. (%)	K (day-1)		(day-1)	T 1/2 (days)	K (day-1)	T 1/2 (days)	
Naphthalene	1.0	-0.568	. 1	-0.596	1	-0.540	1	
2-Methylnaphthalene	2 1.0	-0.562	1	-0.581	1	-0.543	1	
1-Methylnaphthalene	1.0	-0.532	1	-0.549	1	-0.515	1	
Biphenyl	1.0	-0.510	1	-0.520	1	-0.501	1	
Acenaphthylene	1.0	-0.518	1	-0.519	1	-0.516	1	
Acenaphthene	1.0	-0.577	1	-0.577	1	-0.577	1	
Dibenzofuran	1.0	-0,568	1	-0.573	1	-0.564	1	
Fluorene	1.0	-0.579	1	-0.584	1	-0.575	1	
Phenanthrene	1.0	-0.058	2	-0.076	9	-0.040	17	
Anthracene	1.0	-0.026	27	-0.037	19	-0.016	45	
Carbazole	1.0	-0.539	1	-0.555	1	-0.524	1	
Fluoranthene	1.0	-0.019	36	-0.027	25	-0.011	65	
Pyrene	1.0	-0.016	45	-0.023	30	-0.008	86	
1,2 Benzanthracene	1.0	-0.007	107	-0.011	66	-0.002	285	
Chrysene	1.0	-0.007	102	-0.011	64	-0.003	248	
Benzo-a-pyrene	1.0	NT	NT	NT	NT	NT	NT	
Benzo-ghi-perylene	1.0	NT	NT	NT	NT	NT	NT	

Table 38. Kinetic data for PAH degradation/transformation in Grenada soils. (continued)

			T 1/2 (days)	95%	Confidenc	e Interval	
				Lower Limit		Upper Limit	
Compounds	Loading Dry Wt. (%)	K (day-1)		(day-1)	T 1/2 (days)	K (day-1)	T 1/2 (days)
Naphthalene	3.0	ND ^b	ND	ND	ND	ND	ND
2-Methylnaphthalene	3.0	ND	ND	ND	ND	ND	ND
1-Methylnaphthalene	3.0	ND	ND	ND ·	ND	ND	ND
Biphenvl	3.0	-0.523	1	-0.524	1	-0.522	1
Acenaphthylene	3.0	ND	ND	ND	ND	ND	ND
Acenaphthene	3.0	ND	ND	ND	ND	ND	ND
Dibenzofuran	3.0	-0.006	116	-0,009	75	-0.003	248
Fluorene	3.0	ND	ND	ND	ND	ND	ND
Phenanthrene	3.0	-0.095	7	-0.351	2	NT	NT
Anthracene	3.0	-0.087	8	-0.348	2	NT	NT
Carbazole	3.0	ND	ND	ND	ND	ND	ND
Fluoranthene	3.0	-0.033	21	-0.049	14	-0.017	42
Pyrene	3 0	-0.033	21	-0.036	19	-0.029	24
1.2 Renzanthracene	3.0	-0.030	23	-0.038	18	-0.022	31
Chrysene	3.0	-0.010	72	-0.016	43	-0.010	72
Benzo-a-ovrene	3.0	NT	NT	NT	NT	NT	NT
Benzo-ghi-perylene	3.0	ND	ND	ND	ND	ND	ND

Table 38. Kinetic data for PAH degradation/transformation in Grenada soils. (continued)

				95% Confidence Interval					
				Lower Limit		Upper Limit			
Compounds	Loading Dry Wt. (%)	K (day-1)	T 1/2 (days)	K (day-1)	T 1/2 (days)	K (day-1)	T 1/2 (days)		
Naphthalene	0.33	-0.542	1	-0.551	1	-0.533	1		
2-Methylnaphthalene	0.33	-0.490	ī	-0.513	1	-0.467	1		
1-Methylnaphthalene	0.33	-0.490	ĩ	-0.514	1	-0.466	1		
Bipheny l	0.33	-0.166	4	-0.626	1	NT ^a	NT		
Acenaphthylene	0.33	-1.551	1	-0,586	1	NT	NT		
Acenaphthene	0.33	-0.523	1	-0.532	1	-0.515	1		
Dibenzofuran	0.33	-0.544	1	-0.548	1	- 0.537	1		
Fluorene	0.33	-0.544	1	-0.548	1	-0.539	1		
Phenanthrene	0.33	-0.136	5	-0.284	2	NT	NT		
Anthracene	0.33	-0.180	4	-0.407	2	NT	NT		
Carbazole	0.33	D D	ND	ND	ND	ND	ND		
Fluoranthene	0.33	-0.017	41	-0.036	19	NT	NT		
Pyrene	0.33	-0.013	53	-0.022	32	-0.003	205		
1,2 Benzanthracene	0.33	-0.005	139	-0.012	58	NT	NT		
Chrysene	0.33	NT	NT	NT	NT	NT	NT		
Benzo-a-pyrene	0.33	ND	ND	ND	ND	ND	ND		
Benzo-ghi-perylene	0.33	ND	ND	ND	ND	ND	ND		

Table 39. Kinetic data for PAH degradation/transformation in Meridian soils.

^aNT = no transformation observed.

 b_{ND} = not detected.

				95% Confidence Interval					
				Lower L	.imit	Upper L	imit		
Compounds	Loading Dry Wt. (%)	K (day-1)	T 1/2 (days)	K (day-1)	T 1/2 (days)	K (day-1)	T 1/2 (days)		
laphthalene	1.0	-0.108	6	-0.285	2	NT	NT		
² Methy Inaphthalene	1.0	-0.096	7	-0.272	3	NT	NT		
1-Methylnaphthalene	1.0	-0.091	8	-0.264	3	NT	NT		
⁸ ipheny1	1.0	-0.086	8	-0.026	27	NT	NT		
Acenaphthvlene	1.0	-0.083	8	-0.256	3	NT	NT		
Acenaphthene	1.0	-0.101	7	-0.028	25	NT	NT		
ibenzofuran	1.0	-0.109	6	-0.289	2	NT	NT		
luorene	1.0	-0.107	7	-0.286	2	NT	NT		
henanthrene	1.0	-0.018	38	-0.044	16	NT	NT		
Athracene	1.0	-0.025	28	-0.161	4	NT	NT		
arbazole	1.0	-0.096	7	-0.273	3	NT	NT		
luoranthene	1.0	ŇT	NT	NT	NT	NT	NT		
Yrene	1.0	NT	NT	NT	NT	NT	NT		
.2 Benzanthracene	1.0	-0.048	15	-0.146	5	NT	NT		
hrvsene	1.0	-0.043	16	-0.142	5	NT	NT		
enzo-a-ovrene	1.0	NT	NT	NT	NT	ŃT	NT		
Senzo-ghi-perylene	1.0	NT	NT	NT	NT	NT	NT		

Table 39. Kinetic data for PAH degradation/transformation in Meridian soils. (continued)

				95% Confidence Interval					
				Lower L	.imit	Upper Limit			
Compounds	Loading Dry Wt. (%)	K (day-1)	T 1/2 (days)	K (day-1)	T 1/2 (days)	K (day-1)	T 1/2 (days)		
Naphthalene	3.0	-0,606	· 1	-0.637	1	-0.574	1		
2-Methylnaphthalene	3.0	-0.577	1	-0.586	1	-0.567	1		
1-Methylnaphthalene	3.0	-0,557	1	-0.561	1	-0.553	1		
Biphenyl	3.0	-0.516	1	-0.520	1	-0.512	1		
Acenaphthylene	3.0	-0.539	1	-0.547	1	-0.531	1		
Acenaphthene	3.0	-0,124	6	-0.267	3	NT	NT		
Dibenzofuran	3.0	-0.070	10	-0.221	3	NT	NT		
Fluorene	3.0	-0.082	8	-0.253	3	NT	NT		
Phenanthrene	3.0	-0.086	8	-0.242	3	NT	NT		
Anthracene	3.0	-0.124	6	-0.274	3	NT	NT		
Carbazole	3.0	-0.585	1	-0.592	1	-0.579	1		
Fluoranthene	3.0	-0.008	90	-0.019	37	NT	NT		
Pyrene	3.0	NT	NT	NT	NT	NT	NT		
1.2 Benzanthracene	3.0	-0.060	12	-0.206	3	NT	NT		
Chrysene	3.0	-0.062	11	-0.216	3	NT	NT		
Benzo-a-ovrene	3.0	NT	NT	NT	NŤ	NT	NT		
Benzo-ghi-perylene	3.0	ND	ND	ND	ND	ND	ND		

Table 39. Kinetic data for PAH degradation/transformation in Meridian soils. (continued)

				95% Confidence Interval						
		K (day-1)	T 1/2 (days)	Lower L	Lower Limit		Upper Limit			
Compounds	Loading Dry Wt. (%)			K (day-1)	T 1/2 (days)	K (day-1)	(days)			
Naphthalene 2-Methylnaphthalene 1-Methylnaphthalene Biphenyl Acenaphthylene Acenaphthene Dibenzofuran Fluorene Phenanthrene Anthracene Carbazole Fluoranthene Pyrene 1.2 Benzanthracene Chrysene Benzo-a-pyrene Benzo-ghi-perylene	0.33 0.33	-0.523 -0.518 -0.492 -0.490 -0.150 -0.270 -0.271 -0.277 -0.178 -0.164 -0.174 -0.024 -0.122 -0.016 -0.260 ND ND	1 1 1 5 3 3 3 4 4 4 29 6 43 3 ND ND	-0.529 -0.522 -0.505 -0.496 -0.565 -0.422 -0.421 -0.434 -0.258 -0.248 -0.276 -0.035 -0.221 -0.106 -0.391 ND ND	1 1 1 2 2 2 3 3 3 20 3 7 2 ND ND	-0.518 -0.514 -0.479 -0.485 -0.266 -0.119 -0.121 -0.120 -0.097 -0.081 -0.072 -0.013 -0.023 NT ^a -0.129 ND	1 1 1 3 6 6 6 7 9 10 53 30 NT 5 ND ND			

Table 40. Kinetic data for PAH degradation/transformation in Wiggins soils.

^aNT = no transformation observed.

ND = not detected.

				95% Confidence Interval					
	Loading			Lower L	.imit	Upper Limit			
Compounds	Dry Wt. (%)	K (day-1)	T 1/2 (days)	(day-1)	T 1/2 (days)	K (day-1)	T 1/2 (days		
Naphthalene	1.0	-0.117	6	-0.267	3	NT	NT		
2-Methylnaphthalene	2 1.0	-0.119	6	-0.263	3	NT	NT		
1-Methylnaphthalene	1.0	-0.266	3	-0.412	2	-0.119	6		
Biphenyl	1.0	-0.258	3	-0.391	2	-0.125	6		
Acenaphthylene	1.0	-0.253	3	-0.384	2	-0.123	6		
Acenaphthene	1.0	-0.017	41	-0.143	5	NT	NT		
Dibenzofuran	1.0	-0.012	58	-0.029	24	NT	NT		
Fluorene	1.0	-0.012	58	-0.032	22	NT	NT		
Phenanthrene	1.0	-0.012	58	-0.310	2	NT	NT		
Anthracene	1.0	NT	NT	NT	NT	NT	NT		
Carbazole	1.0	NT	NT	NT	NT	NT	NT		
Fluoranthene	1.0	-0.012	58	-0.023	30	-0.001	693		
Pvrene	1.0	NT	NT	NT	NT	NT	NT		
1.2 Benzanthracene	1.0	-0.001	693	-0.007	99	NT	NT		
Chrysene	1.0	NT	NT	NT	NT	NT	NT		
Benzo-a-ovrene	1.0	NT	NT	NT	NT	NT	NT		
Benzo-ghi-perylene	1.0	-0.525	1	-0.544	1	-0.506	1		

Table 40. Kinetic data for PAH degradation/transformation in Wiggins soils. (continued)

				95%	95% Confidence Interval					
				Lower	Limit	Upper	Upper Limit			
Compounds	Loading Dry Wt. (%)	K (day-1)	T 1/2 (days)	K (day-1)	T 1/2 (days)	K (day-1)	T 1/2 (days)			
Naphthalene 2-Methylnaphthalene 1-Methylnaphthalene Biphenyl Acenaphthylene Acenaphthene Dibenzofuran Fluorene Phenanthrene Anthracene Carbazole Fluoranthene Pyrene 1,2 Benzanthracene Chrysene	3.0 3.0 3.0 3.0 3.0 3.0 3.0 3.0 3.0 3.0	-0.202 -0.201 -0.155 -0.564 -0.542 -0.040 -0.025 -0.030 -0.034 -0.014 -0.013 -0.015 -0.002 -0.005 -0.001	3 3 4 1 1 17 28 23 20 50 53 46 347 139 7	-0.315 -0.311 -0.280 -0.565 -0.548 -0.059 -0.043 -0.048 -0.052 -0.023 -0.020 -0.032 -0.020 -0.032 -0.007 -0.011 -0.007	2 2 1 1 12 16 14 13 30 35 22 99 63 99	-0.089 -0.091 -0.031 -0.563 -0.536 -0.022 -0.007 -0.013 -0.016 -0.005 -0.006 NT NT NT NT	8 8 22 1 1 32 99 53 43 139 116 NT NT NT NT			
Benzo-a-pyrene Benzo-ghi-perylene	3.0 3.0	-0.190 ND	4 ND	-0.376 ND	ND	-0.004 ND	ND			

Table 40. Kinetic data for PAH degradation/transformation in Wiggins soils. (continued)

				95% Confidence Interval						
				Lower Limit		Upper	Limit			
Site	Loading Dry Wt. (%)	K (day-1)	T 1/2 (days)	K (day-1)	1 1/2 (days)	K (day-1)	(days)			
Meridian	3.0	NT ^a	NT	NT	NT	NT	NT			
	1.0	-0.0096	72	-0.0176	30	-0.0015	462			
	0.3	-0.0152	43	-0.0206	34	-0.0115	60			
Grenada	3.0	-0.0335	21	-0.0482	14	-0.0188	37			
	1.0	-0.0131	53	-0.0263	26	NT	NT			
	0.3	-0.0152	46	-0.0178	39	-0.0125	55			
Columbus	3.0	-0.0018	385	-0.0028	248	-0.0009	758			
	1.0	NT	NT	NT	NT	NT	NT			
	0.3	-0.0006	1087	-0.0021	334	NT	NT			
Wiggins	3.0	-0.0066	105	-0.0200	35	NT	NT			
	1.0	-0.0076	91	-0.0235	29	NT	NT			
	0.3	-0.0060	116	-0.0217	32	NT	NT			

abl	e	41.	Kinetic	data	for	PCP	degradation/transformation	i in	site	soils.
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 $a_{\rm NT}$ = no transformation observed.

				9	5% Confide	nce Interval	
				Lower L	<u>imit</u>	Upper Limit	
Site	Loading Dry Wt. (%)	K (day-1)	T 1/2 (days)	K (day-1)	T 1/2 (days)	K (day-1)	T 1/2 (days)
Meridian	3.0	NT ^a	NT	NT	NT	NT	NT
	1.0	NT	NT	NT	NT	NT	NT
	0.3	-0.1251	6	-0.1959	4	-0.0543	13
Grenada	3.0	-0.0152	46	-0.0178	39	-0.0125	55
	1.0	-0.01973	35	-0.03935	18	-0.00011	6301
	0.3	-0.0006	1161	-0.0053	130	NT	NT
Columbus	3.0	NT	NT	NT	NT	NT	NT
	1.0	-0.001	.663	-0.004	160	NT	NT
	0.3	NT	NT	NT	NT	NT	NT
Wiggins	3.0	NT	NT	NT	NT	NT	NT
	1.0	NT	NT	NT	NT	NT	NT
	0.3	-0.0009	766	-0.0023	301	NT	NT

Table 42. Kinetic data for OCDD degradation/transformation in site soils.

 $^{a}NT = no transformation observed.$

	Londing	Colu	mbus	Gre	enada	Meri	dian	Wigg	ins
Media	Drý Wt. (%)	Start	Peak	Start	Peak	Start	Peak	Start	Pea
ρ	0.3	.07A	.15A	.05A	4.40B	.31A	2.10B	.22A	5.108
	1.0	.02A	.10A	.04A	6.90B	.33A	4.10B	.09A	6.108
	3.0	.01A	.14B	.05A	4.80B	.24A	5.10B	.05A	4.10
С	0.3	.50A	.50A	.84A	9.40B	2.70A	3.50A	.40A	4.20B
	1.0	.47A	2.00B	1.20A	7.60B	2.20A	3.80B	.20A	3.00°
	3.0	.50A	2.00B	.70A	7.10B	2.90A	4.60B	.26A	3.90
C+P	0.3	.09A	.85B	.06A	4.40B	.29A	2.60B	.27A	5.508
	1.0	.01A	.39B	.04A	8.20B	.30A	4.00B	.10A	6.40
	3.0	.01A	.11B	.04A	5.80B	.23A	4.60B	.05A	4.70
NA	0.3	.67A	2.60B	.48A	8.40B	3.20A	3.40A	.42A	5.10 [°]
	1.0	.88A	2.10B	.92A	6.90B	3.00A	4.15A	.39A	5.80 [°]
	3.0	.74A	1.70B	.52A	9.60B	3.60A	4.80B	.05A	4.708
PDA	0.3	.90A	2.40B	1.10A	10.008	3.20A	3.20A	.51A	5.70
	1.0	.91A	2.50B	1.40A	9.108	2.98A	4.50B	.29A	6.10
	3.0	.57A	2.90B	1.10A	9.508	3.30A	6.40B	.27A	5.30
PDAA	0.3	.05A	.05A	.04A	1.108	.13A	.17A	.05A	.16
	1.0	.02A	.04A	.04A	.708	.13A	.13A	.05A	.11
	3.0	.01A	.05B	.02A	.308	.10A	.19B	.07A	.07

Table 43. Starting and peak microbe counts.^a

^aStarting and peak microbe count means within a site, media, and loading rate are not different by Duncan's Multiple Range Test (P = 0.05) if followed by the same letter.

lives of more than one hundred days. Naphthalene, 2-methylnaphthalene, 1-methylnaphthalene, biphenyl, acenaphthalene, acenaphthene, dibenzofuran, and fluorene have half lives of ten days or less in most cases. Phenanthrene, anthracene, carbazole, and fluoranthene have half lives between ten and one hundred days in most cases. Pyrene, 1,2-benzanthracene, chrysene, benzo-a-pyrene, and benzo-ghi-perylene have half lives greater than one hundred days in most cases. In several cases these last five showed essentially no breakdown within the time frame of the experiment.

The breakdown rates of individual PAH's were apparently related to molecular size and structure, as noted in previous studies. The zero to ten day half life group contained compounds with two aromatic rings, the ten to one hundred day half life group contained compounds with three aromatic rings, and the one hundred plus day half life group contained compounds with four or more aromatic rings. However, some of the larger, most recalcitrant compounds apparently were broken down readily in some situations. This gives hope that even the most persistent PAH's might yield to biological remediation techniques under the right conditions with appropriate microbial populations.

Carbazole, a compound containing a nitrogen bridge between two aromatic rings, varied greatly in persistence in different soils and loadings. This may be due to the nitrogen atom affecting water solubility and other properties of carbazole under varying local oxidation/reduction potentials and pH.

Acenaphthylene and acenaphthene, differing only in the presence or absence of a double bond (and two hydrogens) show the effect of small changes in structure. Acenaphthene had much longer average half life

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than acenaphthylene. Apparently, the double bond is easier to attack, although the single bond in acenapthene also lowers the vapor pressure, possibly affecting the half life by vaporization.

The microbial populations found in the plate counts were not closely related to PAH breakdown, since PAH breakdown was similar at similar concentrations over the four sites, while microbe counts varied.

PCP transformation occurred in all the soils, but was slow in Columbus soil, which was from a site not exposed to PCP treatment wastes. Grenada soil transformed PCP with half lives ranging from one to two months, a quite practical range for land treatment operations. Meridian soil also exhibited rapid transformation rates except at the highest loading rate. Wiggins soil transformed PCP with half lives of three to four months, still an appropriate range for land treatment operations especially considering its deep south location where soil temperatures are high enough for good microbiological activity most of the year. Although the Columbus soil did exhibit some transformation of PCP, the low rates would bring into question the practicality of land treating PCP at that location. However, it is not known what length of time is required to build up a population of microorganisms suitable for rapid degradation of PCP in hitherto unexposed soil. Evidently, the relatively short time frame of these experiments was insufficient for the Columbus soil, at least. It is likely in most soils with chronic exposure to PCP (which is where PCP disposal by landfarming would be needed) that suitable populations could be induced relatively guickly.

OCDD transformation occurred to some degree in all the soils, but only Grenada soil consistently transformed OCDD at all loadings. Since

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Grenada soil also consistently transformed PCP, a relationship may exist in the potential for a soil to transform these two compounds. Dioxins are widely regarded as being somewhat recalcitrant to biological transformation, but these data indicate the potential for biological treatment. Concentrated sources of dioxins would probably be incinerated, but biological treatment in soil could be very useful for materials such as wood treating wastes that contain low levels of dioxins.

General Discussion

The results of these experiments indicate that PAH's, PCP, and OCDD can be transformed at practically useful rates in soil. Although the variability of the data is relatively large in some cases, the general trend is clear. Land treatment of creosote and PCP wood treating wastes appears to provide a viable management alternative based on treatability data in the soils tested to date. The data variability does support the need for conducting site-specific treatability studies to discern the appropriate operation and management scenario for a given site.

Further study of treatment of OCDD, PCP, and the higher molecular weight PAH's is needed to determine the most advantageous environmental conditions and management techniques for more rapid transformation of these compounds. Many of these compounds were readily transformed in some cases. Therefore, further study may reveal reliable techniques for enhancing land treatment as a practically useful management alternative for these recalcitrant compounds. Since the environmental problems that the wood treating industry has to deal with are almost unlimited, and the resources available to solve these problems are quite limited, a reliable, safe, economical remediation technique such as land treatment is very attractive.

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APPENDIX A

METHODOLOGY

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Process	Method number	Compounds	Comments
Extraction of soil samples	3540	A11	Use 10 g of soil
Extraction of water samples	3520	A11	Use 1000 ml of water
Clean up	3630	A11	Done after methylation of phenols
Analysis	8100	PAH's	For polynuclear aromatic hydrocarbons
Analysis	8040	OCDD+PCP	For chlorinated phenols after methylation and octa- chlorodibenzo-p-dioxin; using an ECD detector
Analysis	8270	A11	Check for all compounds
Analysis	8280		Used for low-level dioxins (penta, hexa, and hepta dioxins)

Table A-1. Analytical procedures for soil and water (U. S. EPA 1986a).

Table A-2. Analytical procedures for sludges.

Process	Procedure		
Water content	ASTM D-95-70		
Organic content	Heating at 600°C for 2 hours in an oxidative atmosphere		
Non-volatile products	Heating at 600 ⁰ C for 2 hours in an oxidative atmosphere		
Organic carbon	Determined by CO ₂ evolution		
Total phenolics	Method 222E Standard Methods for Examination of Water and Wastewater		
Oil and grease	Method 5030 Standard Methods for Examination of Water and Wastewater		
Nitrogen	Micro Kjeldahl followed by digestion with 5% hydrogen peroxide and sulfuric acid; nitrogen was determined colorimetrically using nessierization		
Phosphorous	Determined after digestion colorimetrically using the Fisbe-Subarrow method		
Inorganic chloride	Determined using a chloride specific ion electrode		

Extraction of PCP, PAH's, and OCDD from Soil

Soil (10 g) was mixed with dry sodium sulfate (10 g). (The sodium sulfate had been dried at 400° C for four hours and stored in a desiccator.) The sample was placed in an extraction thimble and 1 ml of an internal standard in methylene chloride was added. The internal standard mixture for high levels consisted of 5,000 ppm of diphenylmethane, 1000 ppm of tribromophenol, and 21 ppm of octachloro-naphthalene. For low levels, a 1 to 10 dilution of the internal standard was used. The extraction thimble was placed in the Soxhlet unit along with 300 ml of pesticide grade methylene chloride and boiling chips.

The soil in the Soxhlet unit was extracted for 16 hours with a minimum recycle rate of 5/hour. The extraction units were cooled and transferred to a Kuderna-Danish unit and condensed to a volume of approximately 3 ml.

The condensed extract was diluted to exactly 5 ml and aliquots were taken for OCDD and PCP and PAH analyses. The remaining solution was stored in a freezer at -27° C in a teflon-lined, screw-cap vial.

Clean-up and Determination of PAH's and PCP in Soil Extracts

Silica gel was activated at 130° C for 16 hours (100-120 mesh Davison Chemical Grade 923 or equivalent) in a beaker covered with foil. The silica gel was stored in an air-tight desiccator and redried every two weeks. The columns (10 mm i.d.) were packed using 9 grams of activated silica gel. The silica gel was packed into the column with gentle tapping. The column was pre-eluted with 20 ml of pentane (pesticide grade or HPLC grade). The pentane was allowed to elute until the solvent was just above the silica gel. The silica gel was not allowed to dry before sample addition.

An aliquot of the methylene chloride extract was put in a sample tube. <u>The exact amount depended on the loading amount of creosote or</u> <u>the analysis of previous sample</u>. Three ml of sample was added if the loading rate was less than 0.632% (wt/wt) of creosote on soil or if the previous sample contained less than 6,000 ppm total PAH's.

Diazomethane solution (0.1 ml) was added to the sample tube and mixed with a vortex mixer. An aliquot was added to the column. If a 1-ml aliquot on column was used, 2 ml of methylene chloride was added to the column. A 1 to 3 ml aliqot of 40% methylene chloride/60% pentane was added three times to ensure that all the sample is absorbed on the column. Columns were eluted with 50 ml of the 40/60 mixture and the eluant was collected. The eluant was concentrated to 5 ml by evaporation using a gentle stream of dry air or nitrogen and analyzed using gas chromatography conditions shown below for PAH's.

A 1-ml sample was removed for PCP analysis and stored in a glass teflon-lined crimp-top vial. This sample had to be diluted for GC/ECD analysis. The exact dilution depended on the anticipated concentration of PCP.

Tracor 540 Gas Chromatograph Parameters for PAH Analysis

Column: J and W DB-5 fused silica capillary Length: 30 meters Film thickness: 1.00 um Inside diameter: 0.32 mm Injector temperature: 325°C Oven temperature program: 4 minutes to 40°C, then 6°C per minute for 15 minutes to 325°C Carrier gas: Helium; Pressure: 12 psi FID temperature: 325°C Hydrogen flow: 60 cc/min Air flow: 400 cc/min Nitrogen makeup: 40 cc/min Injection: 2 μ l splitless, vent after 1.5 min. Amplifier range: xl

Tracor 540 GC Parameter for PCP Analysis

Column: 6 ft x 2 mm i.d. glass packed with 3% SP-2250 on 100/120
 mesh supelcoport
Carrier gas: Ar/CH₄ at 10 cc/min
Injector: 250°C
Oven: 220°C
Detector: 350°C
ECD detector makeup gas: 95% argon/5% methane at 60 cc/min.

<u>Clean-up and Determination of Octachlorodibenzo-p-dioxin in Soil (MSU 1984)</u>

The analysis of OCDD in soil presented two significant problems which had to be dealt with in order to obtain reliable results. First, an extraction procedure had to be used which would be highly efficient in removing OCDD from the sample matrix. This was especially important, since the anticipated concentration of OCDD in the soil was in the parts-per-billion range. Secondly, the majority of the compounds which co-extracted with OCDD were likely to be several orders of magnitude higher in concentration than OCDD. A clean-up technique had to be used which allowed the concentration of OCDD with minimal chemical interference.

Method Summary--Methylene chloride Soxhlet extraction was found to be very efficient in the removal of OCDD from a soil matrix (U. S. EPA 1983). Thus, an aliquot of soil extract from the PAH analysis, which uses the same extraction procedure, was considered to be adequate and also would save analysis time. For our purposes, the removal of the majority of chemical interferences could be accomplished by a modification of two column clean-up techniques recommended by EPA for 2,3,7,8-TCDD analysis (U. S. EPA 1983). An elution profile and recovery were determined for this modified column clean-up and were found to be quite adequate (Mississippi State 1984).

Materials and Supplies--

Basic alumina, type WB-5, Activity Grade I, Sigma Chemical Co. or equivalent.

Silica gel, 100/200 mesh, Fisher Scientific Co. or equivalent.

5 ml disposable pipet, Scientific Products Co.

Silane treated glass wool, Supelco, Inc.

9" disposable Pasteur pipets, Scientific Products Co.

10 ml graduated cylinder, Pyrex.

Small funnel with a cut latex bulb attachment.

Disposable 1 ml serological pipet, Scientific Products Co.

Compressed air with regulator and manifold.

Water bath.

Benzene (Burdick and Jackson distilled in glass).

OCDD for standards, Analabs.

Gas chromatograph equipped with ECD and a 6-ft x 2-mm i.d. glass column packed with 3% SP-2250 on 100/120 mesh supelcoport.

Procedure--

- Before use, the silica gel and basic alumina were activated for 16-24 hours at 130° C in a foil-covered glass container.
- A small plug of glass wool was placed in the bottom of a 5-ml pipet.
- A funnel with a cut latex bulb attached was placed on the pipet and 2 ml of basic alumina (bottom) and 2 ml of silica gel (top) were added to the pipet.
- The column was pre-rinsed with two 4-ml portions of Benzene which was then discarded.

A 10-ml volumetric flask was placed under the column. Before clean-up, the methylene chloride extract was exchanged with benzene by blowing down the methylene chloride to dryness with dry air in a 50° C water bath and adding 1 ml of benzene.

The benzene extract was placed on the column.

- After the sample extract had flowed into the silica gel layer, 4 ml of benzene was added to the column.
- All of the eluate was collected until the column stopped dripping.
- The eluate was diluted to 10 ml with benzene and a 1 μ l sample was injected on the Tracor 540 GC/ECD using the following conditions:

Oven: 280°C; Injector: 330°C; Detector: 350°C

Quality Assurance Program for Soil Extraction and Analysis

Four types of internal checks were used to monitor the accuracy of the soil extraction and analytical procedures.

Blanks--This control was used to monitor the glassware, solvents, and the solid supports (silica gel and alumina) background levels. The blank was processed exactly the same way as the samples except no soil was used during the Soxhlet extraction. Diphenylmethane, 2,4,6tribromophenol, and octachloronaphthalene were added to the extracts as an internal standard.

Spike Samples--Standard solutions of PAH's, PCP, and OCDD were prepared using the best standards available (purity = 99% or better) in methylene chloride. A sample of the standard solution was added to the soil before Soxhlet extraction. The sample was extracted and cleaned up using the normal procedures. The values of the spiked sample were used to determine the recovery values for the individual compounds. Diphenylmethane, 2,4,6-tribromophenol, octachloronaphthalene were used as internal standards. All standards were prepared using a Mettler 5-place analytical balance. Each time a standard was prepared, the weight, date, and standard number were recorded, and the balance was checked with standard weights (Class S - National Bureau Standards).

Standard Solutions for Gas Chromatography Calibration--A standard solution of PAH's containing the 16 compounds of interest was prepared. It contained an internal standard (diphenylmethane). Standard solutions were also made for the PCP and octachlorodibenzo-p-dioxin and analysis with the corresponding internal standards 2,4,6-tribromophenol and octachloronaphthalene. A minimum of three concentration levels was used for each compound.

Blind Samples--Blind samples containing EPA standard reference materials (Quality Assurance Branch EMSL-Cincinnati, U. S. EPA) were diluted by the Quality Control Officer (Dr. Hamid Borazjani) and analyzed.

GC/MS Analysis--A part of each sludge sample after homogenizing (approximately 1 gram) was weighed to three significant figures, mixed with an equal weight of anhydrous sodium sulfate and extracted for 16 hours with 300 ml of methylene chloride in a Soxhlet extractor. The volume of methylene chloride from each sample was adjusted to 100 ml with a volumetric flask. A 1.00 ml aliquot of each extract was transferred to a screw cap test tube and stored at approximately 4° C prior to GC/MS analysis. The sample weight range and dilution volume were based on prior knowledge of concentrations determined by GC/FID analysis.

The GC was a Carlo Erba fitted with a J and W DB-5 capillary column [0.25 μ m film thickness and 30 m (1) by 0.25 mm (i.d.)]. After sample injection the GC was operated at 70°C for 2 minutes and

then programmed to 280° C at 6 deg/min and from 280° to 320° C at 12 deg/min. The GC oven temperature was kept at 320° C for 20 minutes. The injector and transfer line temperatures were 320° and 280° C, respectively.

The mass spectrometer (Kratos MS80RFA) was operated in the electron impact mode (70 eV) with a source temperature of 250° C. After a 6.0minute delay for elution of the solvent peak, mass spectral data were acquired with a scan rate of 1 sec/dec for 54.0 minutes. Two standard solutions (10 µg/ml and 200 µg/ml) containing known concentrations of selected analytes were used to establish instrument response factors. The concentration of each compound in solution was reported by the DS-90 data system and the concentration in sludge was calculated as follows:

 $C \mu g/g = \frac{100 \text{ ml x } c \mu g/\text{ml}}{W}$

Here, C = concentration of each compound in sludge ($\mu g/g$); 100 = dilution volume, c = concentration of each compound in the sample extract, and W = dry weight of the sludge sample in grams.

Site and Soil Characterization

Soil profiles were examined at each site in freshly excavated pits and they were described and sampled using standard methods (Soil Survey Staff, 1951). Soil morphological descriptions included horizonation, Munsell color, texture, horizon boundaries, consistency, coarse fragments, root distribution, concretions and pedological features. Each horizon was sampled for laboratory analyses. Bulk density was determined on major horizons using the non-disturbed core method (Blake, 1965). Saturated hydraulic conductivity was determined on non-disturbed cores using the constant heat method (Klute, 1965). Soil moisture retention was determined on non-disturbed cores using a pressure membrane apparatus (Richards, 1949).

Soil samples were air-dried in the laboratory, crushed with a wooden rolling pin, and sieved through a 10-mesh sieve to remove fragments larger than 2 mm (USDA, 1972). Particle size distribution was determined by the hydrometer method and sieving (Day, 1965). Organic matter was determined by a wet combustion procedure (Allison, 1935). Extractable acidity was determined by the barium chloridetriethanolamine method (Peech, 1965). Exchangeable aluminum was determined in KCl extractions following the procedure of Yuan (1959). Exchangeable cations were extracted with neutral 1 <u>N</u> NH₄OAc and determined by atomic absorption spectrophotometry (USDA 1972). Soil pH was measured in water and 1 <u>N</u> KCl using a 1:1 soil-to-liquid ratio. Electrical conductivity was determined in saturated paste extracts using a Wheatstone conductivity cell. Total sulfur was determined on soil samples ground to pass a 60-mesh sieve in a LECO Sulfur Analyzer using an induction furnace and I.R. detection.

The clay fraction (<2 mm) was separated by centrifugal sedimentation using Calgon as a dispersing agent. Clays were K-saturated, Mg-saturated, and glycerol-solvated for x-ray diffraction analysis. The clay fraction was analyzed with a Norelco Geiger counter spectrophotometer using Cu K radiation and a Ni filter. Minerals were identified based on comparison of diffraction spacings and frequencies to standard minerals as indicated by Jackson (1956), Carrol (1970), and Dixon and Weed (1978). Relative estimates of the amounts of clay minerals present were based on peak area measurements with corrections for Lorentz polarization at peaks greater or equal to 14 Å.

Transformation/Degradation Using a Standard Creosote/PCP Mixture: Experiment I

Wet soil was spread upon a new sheet of plastic and air-dried for 24 hours or longer until the moisture content was reduced. The dried soil was stored in clean glass containers that had been labeled with the soil source, the collection day, and a number. A sample of each new soil was sent to Delta Labs, Inc., for analysis of soil parameters. nitrogen, phosphorus, organic carbon, and inorganic metals; pH and chloride ion was determined in-house. The soil was sieved just before use to remove coarse plant materials from the soil, and the moisture content was determined. Spiked soil samples were prepared using the following procedure: Soil samples (50.0 g/beaker) were accurately weighed into 10 beakers. Known amounts of creosote and/or technical grade pentachlorophenol were added into each beaker. Technical grade PCP was dissolved thoroughly in methylene chloride or methanol before being added to the soil in the beaker. Then contents of all ten beakers were combined and mixed for 2 hours in a clean glass jar using a sample rotator with a minimum of 50 revolutions/minute. The dual procedure for mixing was found to give more uniformly mixed material. Soil moisture was adjusted to 70% of water-holding capacity by adding deionized H₂O into the soil when mixing was finished. The same mixing procedure was repeated for controls.

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Two test units were set up for each site. One unit was a control (0%), and one was loaded at 1% with the standard creosote/PCP mixture. Each unit consisted of a brown glass container with a lid (baking dish) containing 500 g of soil (dry weight). Soil moisture content was adjusted to 70% of water-holding capacity, and the container's weight was determined. The accurate weight of the unit was important since this value was used to maintain a proper moisture content during the study. The test units were put into a constant temperature room maintained at $22^{\circ} \pm 2^{\circ}$ C for the duration of the study.

Each test was begun by hand stirring the samples and removing two separate 20 g samples of soil (air-dry weight) from each of the units. One sample was used to analyze for PAH's, PCP, and octachlorodibenzop-dioxin using the procedure described in a later section of this report. The second sample was used for bacterial counts, pH and chloride ion analysis.

The moisture content of each unit was adjusted weekly to 70% by adding deionized water. The soil was aerated by thoroughly mixing the total contents of each unit every 7 days.

The first samples were taken after 30 days (20 g dry weight) and analyzed for PAH's, PCP, and OCDD. Further samples were taken every 30 days until the experiment was complete.

Soil from sites at Gulfport, Grenada, and Wiggins were loaded initially and at 30 and 60 days. Soil from sites at Atlanta, Meridian, and Wilmington were loaded intially and at 30 days, while the soil from sites at Columbus and Chattanooga were loaded only at day 0. A change was made in loading frequency because data for several sites indicated that the bacteria at the sites were readily acclimated with one loading.

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Kinetic data needed to calculate the half lives, assuming first order kinetics, were taken after the final loading and over a 60-120 day period.

No organic or inorganic additions were made to the soil during the initial set of experiments. The parameters measured were:

- microbial plate counts
- pentachlorophenol
- major PAH's contained in creosote

The soil microflora were measured using five different media. The total amounts of bacteria, acclimated bacteria, and fungi were determined using various media. The same media that were used to count bacteria (PDA) were amended with creosote (PDA-C), pentachlorophenol (PDA-P), a combination of creosote and PCP (PDA-PC), and PDA with antibiotics to count fungi (PDA-AA). Because of the very low counts of fungi and because their population counts did not change appreciably during the studies, only the results from the bacteria and acclimated bacteria are reported.

Transformation/Degradation of Site Specific Sludges: Experiment II

In this phase of the study, three different loading rates in soil were studied--0.3%, 1.0%, and 3.0%--based on the total dry weight of solids. A single loading was used instead of multiple loading, and three replications of each soil and loading rate combination were used. Chicken manure was added to all soil at 4% by weight. Sludges from Columbus did not contain PCP, so in order to get information on the rates of degradation of PCP with this soil type, 128-3000 ppm of PCP were added to the Columbus soils. The parameters measured were bacteria, fungi, actinomycetes, acclimated bacteria, pentachlorophenol, major PAH's in creosote, and octachlorodibenzo-p-dioxin. A control sample of soil from eachsite which contained no added sludges or PCP was used as a control for the plate counting procedures and to determine the background levels of PCP, PAH's, and OCDD. Although technical grade PCP contains traces of two other series of dioxins, their levels are extremely low (less than 5% of the octachlorodibenzo-p-dioxin levels). Because of time and resource restraints, it was not possible to monitor trace level dioxins as part of this study.

All other experimental methods, with the exception of the addition of chicken manure to the soil (discussed below) were the same as in Experiment I.

<u>Rationale for the Addition of Chicken Manure to Soil in the</u> <u>Degradation/Transformation Studies</u>

During the course of this series of experiments, the data generated reemphasized the importance of soil organic matter in facilitating the microbial transformation of applied organic wastes. Since the ultimate goal of these studies was to establish an operating landtreatment test facility, the decision was made to maximize the operating effectiveness and efficiency of the facility by amending the experimental soils with an animal manure. This amendment accomplished several objectives. The manure furnished: (1) a carbon source for potential cometabolism, which has been found in at least some instances to be an important component of the transformation process; (2) both major and minor nutrients; and (3) a wide variety of microbes that were potentially important biodegraders. Also, added organic matter should markedly decrease mobility of hazardous constituents in organic applied wastes, which is highly desirable in a landtreatment operation. Although other animal manures might serve as well, chicken manure was chosen for study because it is readily available in many parts of the United States. A typical analysis of the chicken manure used in this study is given below:

> Total organic carbon = 8.97% Total nitrogen = 1.35% Total phosphorous = 0.12%

A comparison between bacteria counts of four of the soils used in this study was done before and after manure addition. No PCP or creosote was added to the soil (0% controls) and the bacteria counts were determined in soil 30 days after manure loading. The results (Table A-3) indicate a large increase in both the total bacteria and the acclimated bacteria in the soil with added chicken manure.

Microbiological Procedures

The media used for this study were potato dextrose agar, PDA (Difco Laboratories, Detroit, Michigan), 39 g in one liter of deionized water, PDA amended with 5 mg/L of technical-grade pentachlorophenol [PDA-P] (Vulcan Materials Company, Wichita, Kansas), PDA amended with 10 mg/L of whole creosote [PDA-C], PDA amended with a combination of 5 mg/L of pentachlorophenol and 10 mg/L of whole creosote [PDA-CP], PDA amended with antibiotics--120 mg/L of streptomycin sulfate (Nutritional Biochemical, Cleveland, Ohio) and 30 mg/L of chlorotetracycline hydrochloride (Nutritional Biochemical, Cleveland, Ohio) [PDAA], and actinomyces broth (Difco Laboratories, Detroit, Michigan) [ACA], 57 g in one liter of deionized water amended with 15 g of Difco agar and 30 mg/L of Pimaricin. The PDA was autoclaved for 20 minutes at 15 psi and 121°C and then cooled to 55°C. Both creosote and pentachlorophenol were

	Total bacter (million counts/	ia counts gram of soil)	Acclimated bacteria counts ^b (million counts/gram_of_soil)		
Site	Before addition	After addition	Before addition	After addition	
Gulfport	1.13	4.50-7.20	0.07	0.50-0.61	
Wiggins	0.41	3.10-4.50	0.12	0.64-2.30	
Columbus	1.25	2.80-3.10	0.25	0.14-0.35	
Meridian	1.10	3.10-4.20	0.09	0.48-0.92	

Table A-3. Bacteria levels in four soils at 0% loading before and after addition of chicken manure^a.

^aThese soils were 0%-loaded, and counts were taken 30 days after addition of chicken manure.

^bBacteria acclimated to PCP and PAH's.

dissolved thoroughly in methyl alcohol and added to cooled PDA. The antibiotics were added to the cooled liquid medium before pouring into petri dishes. The pH of the media was adjusted to 6.9 to 7.1 before autoclaving. Twenty-five ml of PDA, PDA-C, PDA-P, PDA-CP, PDAA, and ACA were poured into disposable petri plates and were allowed to solidify.

For colony counts, triplicate samples of loaded and non-loaded soils were air-dried for 24 to 28 hours under a sterilized transfer hood. The air-dried soil was then screened with a 400 mesh sieve. Serial dilutions were made by using sterilized screened soil. Three 20-mg soil samples were weighed out from treated and non-treated soil for each medium at each sampling date. A modified Anderson sampler (Butterfield et al., 1975, 1977; Warcup, 1950) was used to distribute the soil on the agar. Three 20-mg samples were distributed over each medium for each treatment. Colonies were counted after 24 to 48 hours of incubation at 28^oC. A Darkfield Quebec Colony Counter (AO Scientific Instrument, Keene, New Hampshire) was used to count the number of colonies on each plate.

The number of counts recovered on PDA plates provided an estimate of the total number of bacteria per gram of dry soil. On creosotecontaining plates, it represented the approximate number of bacteria per gram of dry soil that were acclimated to creosote; on PCP-containing plates, it represented the approximate number of bacteria per gram of dry soil that was acclimated to pentachlorophenol; on PDA-CP plates, it represented the approximate number of bacteria per gram of dry soil that was acclimated to both creosote and pentachlorophenol; on PDAA plates, it represented the approximate number of fungi per gram of dry soil; and on ACA plates, it represented the approximate number of actinomycetes per gram of dry soil.

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Statistical Procedures

Statistical methods were used to help determine estimates of compound half-lives and confidence intervals for individual compounds. Differences in concentration of PCP, PAH, and OCDD between sampling times were evaluated by calculating a linear regression based on first-order kinetics. The slope of the regression line was used to calculate the first-order degradation rates in the soil/sludge mixtures. The half-life of each compound was calculated from the first-order degradation rate. The half-life values for the lower and upper 95 percent confidence intervals were also calculated for PCP, PAH, and OCDD compounds, when waste was applied to soil, to indicate the range of values about the half-life.

If the slope of the first-order regression was non-negative, indicating that no treatment by degradation was observed, or if degradation could not be quantified due to initial low concentration (near or below detection limit), no degradation information was reported in the tables.

The microbiological results for the sludges were analyzed using a complete random design using days as treatments with three replications and three samples for each replication. Duncan's multiple range test was used to compare treatment mean differences at (P = 0.05). Data was processed using the Statistical Analysis System (SAS) of prepackaged programs at VIVC (Barr et al., 1979).

	Sludge (ppm)	Soi 1 (ppb)
Naphthalene 2-Methylnaphthalene 1-Methylnaphthalene Biphenyl Acenaphthylene Acenaphthene Dibenzofuran Fluorene Phenanthrene Anthracene Carbazole Fluoranthene Pyrene 1,2-Benzanthracene Chrysene Benzo(a)pyrene Benzo(ghi)perylene	17 23 17 18 22 18 21 18 27 26 36 35 37 43 46 47 48	220 290 220 240 280 240 270 230 340 330 460 450 480 560 590 610 620
Pentachlorophenol	0.27	27
Octachlorodibenzo-p- dioxin	0.54	54

Table A-4. Detection limits for soil and sludge.

SUMMARY

Eight wood treating plant sites were chosen to study the effectiveness of land treatment for remediation of wood treating wastes. The morphological, chemical, and microbiological parameters of the soil at each site were characterized. Typical wood treating waste sludges from each site were chemically analyzed. Soil samples were taken from each site to study the rate of microbiological breakdown of wood treating waste components. In a preliminary experiment, a synthetic waste was mixed with each soil at 1% of the dry weight of the soil in order to ascertain waste breakdown rates using the same waste for all soils. In a second experiment, waste sludge from each site was mixed with soil from each site at three different loading rates (0.33, 1.0, and 3.0% by weight). Chicken manure was added to the soils at 4% weight. The soils were tested at thirty day intervals to determine microbe populations and amounts of waste compounds remaining. Degradation rates were calculated for PCP, OCDD, and seventeen PAH's.

The general conclusions from this study are that PAH's and PCP are readily degraded in soil systems. PAH's were transformed easily in all the soils tested, but PCP was transformed much more quickly in soils with long term exposure to PCP. Lower molecular weight PAH's and PCP were usually transformed more quickly than higher molecular weight PAH's and PCP. Application of PAH and PCP containing wastes to soil greatly increases the population of PAH and PCP adapted microorganisms in the soil. The results of this study indicate that land treatment is an effective alternative for remediation of PAH and PCP containing wood treating wastes.

APPENDIX E

SUPPLEMENTARY MATERIAL FOR PUMP-AND-TREAT TECHNOLOGY

Dr. Joseph F. Keely, Portland, Oregon

PERFORMANCE EVALUATIONS OF PUMP-AND-TREAT REMEDIATIONS

by

Joseph F. Keely, Ph.D., P.Hg., FAIC/CPC

Introduction

Large expenditures are made each year to prepare for and operate pump-and-treat remediations of groundwater contamination. Regulatory responsibilities require that adequate oversight of these remediations be made possible by structuring appropriate compliance criteria for monitoring wells. The oversight efforts are nominally directed at answering the question: What can be done to show whether a remediation is generating the desired control of the contamination or not? Recently, other questions have come to the forefront, brought on by the realization that pump-and-treat remediations do not function as well as has been presumed: What can be done to determine whether the remediation will meet its timelines or not? and What can be done to determine whether the remediation will stay in budget or not?

Conventional wisdom has it that these questions can be answered by the use of sophisticated data analysis tools, such as computerized mathematical models of ground-water flow and contaminant transport. Computer models can indeed be used to make predictions about future performance, but such predictions are highly dependent on the quality and completeness of the field and laboratory data utilized. The latter is just as true of the use of models for performance evaluations of pump-and-treat remediations, in contrast to the common belief that an accurate performance evaluation can be made simply by comparing data obtained from monitoring wells during remediation to the data generated prior to the onset of remediation. The eye-opener is that historical trends of contaminant levels at local monitoring wells are rendered useless by the extraction and injection wells that are used in pump-and-treat remediations. This is a consequence of the fact that the extraction and injection wells produce complex flow patterns locally, where previously there were comparatively simple flow patterns.

Complex ground-water flow patterns present great technical challenges in terms of characterization and manipulation (management) of the associated contaminant transport pathways. In Figure 1, for example, it can be seen that waters moving along the flowline that proceeds directly into a pumping well from upgradient are moving the most rapidly, whereas those waters lying at the lateral limits of the capture zone (indicated by the bold curved line in Figure 1) move much more slowly. One result is that certain parts of the aquifer are flushed quite well and others are remediated relatively poorly. Another result is that those previously uncontaminated portions of the aquifer that form the peripheral bounds of the contaminant plume may become contaminated by the operation of an extraction well that is located too close to the plume boundary, because the flowline pattern extends downgradient of the well. The latter is not a trivial situation that can be avoided without repercussions by simply locating the



Figure 1 Flowline Pattern Generated by an Extraction Well Ground-water flowlines within the bold curved line are captured by the well. Prior to pumping, the flowlines were straight diagonals (unbounded).

extraction well far enough inside the plume boundary so that its flowline pattern does not extend beyond the downgradient edge of the plume, because doing so results in very poor cleansing of the aquifer between the location of the extraction well and the downgradient plume boundary.

It is not possible to determine precisely where the various flowlines generated by a pump-and-treat operation are located, unless detailed field evaluations are made *during* remediation. Consequently, there is a need for more data to be generated during the remediation (esp., *inside* the boundaries of the contamination plume) than were generated during the entire RI/FS process at a site, and for interpretations of those data to require much more sophisticated tools. Indeed, it might be successfully argued that in most settings one cannot begin to make sense of monitoring well data collected during remediation unless a mathematical model is used to organize and analyze the data.

Monitoring for Remediation Performance Evaluations

Data are collected from monitoring wells during remediations to comply with the terms of a consent decree or an administrative order. The key controls on the quality of these data are the *compliance criteria* that are selected and the *compliance point locations* at which those criteria are to be applied. Ideally, the compliance criteria and the compliance point locations would be selected on the basis of a detailed site characterization to provide information on what is happening, not just downgradient of the plume boundary, but also *inside the plume*. Monitoring within the plume makes it possible to determine which parts of the plume are being effectively remediated and how quickly, so that the remediation wellfield can be managed for greatest efficiency (c.g., reducing the flowrates of extraction wells that pump from relatively clean zones and increasing the flowrates of extraction wells that pump from zones that are highly contaminated). By contrast, the exclusive use of compliance points downgradient of the plume boundary does not allow one to gain any understanding about the behavior of the plume during remediation, save to indicate *out of control* conditions when contaminants are detected.

It should be recognized that there are many kinds of compliance criteria and compliance point locations in use today. The former can be divided into three categories: *chemical*, *hydrodynamic*, and *administrative control*. Chemical compliance criteria are Maximum Concentration Limits (MCL's), Alternate Concentration Limits (ACL's), Detection Limits, and Natural Water Quality. Hydrodynamic compliance criteria are such things as (i) demonstrated prevention or minimization of infiltration through the unsaturated zone, (ii) maintenance of an inward hydraulic gradient at the boundary of a plume of ground-water contamination, and (iii) providing minimum flows in a stream. Administrative control compliance criteria include (i) effective implementation of drilling bans and other access-limiting administrative orders, (ii) proof of maintenance of site security, and (iii) reporting requirements, such as frequency and character of operational and post-operational monitoring. Almost any combination of chemical, hydrodynamic, and administrative control compliance criteria might be appropriate for a specific compliance point, depending on its location.

1. Background Compliance Points

The most widely used kind of compliance point is located a short distance downgradient of the plume. The exact location is chosen so that: (i) it is neither in the plume nor in adjacent areas that may be affected by the remediation, (ii) it is in an uncontaminated portion of the strata through which the plume would migrate if the remediation failed, and (iii) its location minimizes the possibility of detecting other actual or potential sources of contamination (e.g., it is not located too far away, to be relevant to the target site only). Data gathered there serve to indicate *out-of-control* conditions when a portion of the plume escapes the remedial action. The compliance criteria typically specified for this kind of compliance point are Natural Water Quality (Background) or Detection Limits.

2. Public-Supply Compliance Points

Another common kind of compliance point is represented by existing public water supply wells downgradient of a plume. The locations of these points are not negotiable; they are where they are. The significance of their use is in assuring the quality of water delivered to consumers, as it relates to specific contaminants associated with the target site. The compliance criteria typically specified for this kind of compliance point are MCL's, MCLG's, and maintenance of existing quality.

3. Gradient Control Compliance Points

A third kind of off-plume compliance point commonly established is one for determinations of hydraulic gradients. This kind is comprised of a cluster of small diameter wells that have very short screened intervals, and is usually located just outside the perimeter of the plume and along a line running between two plume remediation wells. Water level elevations are measured and used to prepare detailed contour maps from which determinations of the direction and magnitude of the local hydraulic gradients can be made.

4. [Internal] Plume Compliance Points

Less commonly known is the kind of compliance point represented by monitoring wells located within the perimeter of the plume. Most of these are installed during the site investigation phase (prior to the remediation), but others may be added subsequent to implementation of the remediation; they are used to monitor the progress of the remediation within the plume. These can be subdivided into compliance points located on-site (within the property boundary of the facility that contains the source of the plume of contamination), and those located off-site (beyond the facility boundary, but within the plume); the latter kind assumes that the plume has migrated beyond the facility boundary.

Because of its proximity to the source of contamination, and the technical infeasibility of complete removal of the source at many sites, the compliance criteria for an on-site compliance point range from Natural Water Quality to Alternate Concentration Limits (ACL's) that represent the best that can be done cost-effectively. In addition, hydrodynamic compliance criteria are often associated with on-site compliance points; e.g., moisture-content determinations may be used to evaluate the effectiveness of a cap in reducing or eliminating infiltration through contaminated soils in the unsaturated zone. An explicit name for these is on-site plume compliance point. Similarly, one can refer to the remaining compliance points located within the perimeter of the plume as off-site plume compliance points. The compliance criteria applied to these tend closer to Natural Water Quality than is the case on-site, but again are closely tied to technology-driven ACL's; more stringent criteria are usually appropriate, because the source is not included.

5. Interdependencies of Compliance Point Criteria

As discussed in the preceding paragraphs, each kind of compliance point has a specific and distinct role to play in evaluating the progress of a remediation. The information gathered is not limited to chemical identities and concentrations, but includes other observable or measurable items that relate to specific remedial activities and their attributes. In choosing specific locations of compliance points, and criteria appropriate to those locations, it is essential to recognize the interdependency of the compliance criteria for different compliance points. For example, one cannot justify liberal ACL's on-site and have realistic expectations of meeting more stringent ACL's off-site; the facility boundary will not magically dilute the residual contaminants leaving the on-site area after the remedial action ceases operation. Similarly, one cannot expect Background Compliance Points to remain free of contamination if the off-site plume ACL is chosen inappropriately.

In addition to the foregoing, one must decide the following: Should evaluations of compliance data incorporate allowances for statistical variations in the reported values? If so, then what cut-off (e.g., the average value plus two standard deviations) should be used? Should evaluations consider each compliance point independently or use an average? Finally, what method should be to use to indicate that the maximum clean-up has been achieved? The zero-slope method, for example, holds that one must demonstrate that contaminant levels have stabilized at their lowest values prior to cessation of remediation -- and that they will remain at that level subsequently, as shown by a flat (zero-slope) plot of contaminant concentrations versus time.

Though fully justified by technical considerations, the economic burden of intensive sampling at compliance points frequently has been sufficient to undercut attempts to structure appropriate compliance criteria in ground-water contamination remediations. This unfortunate response probably draws strength from the perception that the funds used for performance evaluations of remediations ought to comprise a minor portion of the overall costs, parallel to routine performance audits of industrial wellfield operations. In fact, however, the driving issue in remediations is public health, and the approach to medical problems -- where as much or more money is often spent on diagnostic tests than is spent on the remedy/operation -- offers a more appropriate parallel. The economic concept that flows freely through these mutually complex issues is that one cannot expect positive benefits from decisions that are not supported by detailed information.

Contaminant Behavior and Plume Dynamics

Ground water flows from recharge zones to discharge zones in response to the drop in fluid pressure along that path. The drop in fluid pressure may be represented by water-level elevation contours for ground water that has a constant density, but must be represented by water pressure contours for water having a variable density because fluid pressure is created by the combined effects of elevation, fluid density, and the acceleration of gravity. Additions to the dissolved solids content of water causes an increase in its density. For example, synthetic seawater can be prepared by adding mineral salts to fresh water. Landfill leachate is often so laden with dissolved contaminants that its density approaches that of seawater.





Figure 2 Surface Spill of Chemicals from Storage Drums Spilled fluids initially fill the uppermost soil pores. As much as half of the fluids remain in each pore after drainage.

and also acts as a transportation system for viruses and small bacteria. This gives rise to natural water quality -- a combined chemical, biological, and physical state that may, or may not, be suitable for man's use. Brines and brackish waters are examples where the natural quality of ground water is unsuitable for man's use. It is this same power of water to solubilize earth minerals and the decay residues of plants and animals that causes ground-water contamination when ground water is brought into contact with manmade solids and liquids. Once contaminated, ground water also provides a medium for potentially destructive interactions between contaminants and subsurface formations, such as the dissolution of limestone and dolomite strata by acidic wastewaters. Contaminated ground water has been found in every state of our nation, and is the primary focus of most hazardous waste site cleanups. This fact is underscored by the large number of Superfund ROD's that call for pump-and-treat remediations.



Figure 3 Hydraulic Impacts of Contaminant Sources Injection wells and surface impoundments may release fluids at a high rate, resulting in local mounding of the water table. Many sources release fluids too slowly to cause mounding.

The mechanism by which a source introduces contaminants to ground water has a profound effect on the duration and areal extent of the resulting contamination. Surface spills are often attenuated over short distances (Figure 2), by the moisture retention capacity of surface soils. By contrast, there is much less opportunity for attenuation when the contaminant is introduced below the surface, such as occurs through leaking underground storage tanks, injection wells, and septic tanks.

The hydraulic impacts of some sources of ground-water contamination, especially injection wells and surface impoundments, may impart a strongly three-dimensional character to local flow directions. The watertable mounding that takes place beneath surface impoundments (Figure 3), for instance, is often sufficient to reverse groundwater flow directions locally (so that previously upgradient areas are no longer
upgradient) and commonly results in much deeper penetration of contaminants into the aquifer than would otherwise occur. Interactions with streams and other surface water bodies may also impart three-dimensional flow characteristics to contaminated ground-water (e.g., a losing stream creates local mounding that forces ground-water flow downward). In addition, contaminated ground-water may move from one aquifer to another through a leaky aquitard, such as a tight silt layer that is sandwiched between two sand or gravel aquifers.

As ground water moves, contaminants are transported by advection and dispersion (Figure 4). Advection, or velocity, estimates can be obtained from Darcy's Law, which states that the amount of water flowing through porous sediments is found by multiplying together values of the



Figure 4 Bird's-eye View of Contaminant Plume Spreading Advection causes the majority of plume spreading in most cases. Dispersion adds only marginally to the spreading.

hydraulic conductivity of the sediments, the cross-sectional area through which flow occurs, and the hydraulic gradient along the flowpath through the sediments. The hydraulic conductivities of subsurface sediments vary considerably over small spaces. It is primarily this spatial variability in hydraulic conductivity that results in a corresponding distribution of flow velocities and contaminant transport rates.



Figure 5 Cross-sectional View of Contaminant Plume Spreading Permeability differences between strata cause comparable differences in advection and plume spreading.

The plume spreading effects of spatially variable velocities can be confused with dispersion (Figure 5), if the details of the velocity distribution are not adequately known. Dispersion results from the combination of mechanical and chemical phenomena that cause spreading of contaminants at a microscopic level. The mechanical component of dispersion derives from velocity variations among water molecules travelling through the pores of subsurface sediments (e.g., the water molecules that wet the surfaces of the grains that bound each pore move little or not at all, whereas water molecules passing through the center of each pore move most rapidly) and from the branching of flow into the accessible pores around each grain. By contrast, the chemical component of dispersion is the result of molecular diffusion. At modest ground-water flow velocities, the chemical (or diffusive) component of

dispersion is negligible and the mechanical component creates a small amount of spreading about the velocity distribution. At very slow ground-water flow velocities, such as occurs in clays and silts, the mechanical component of dispersion is negligible and contaminant spreading occurs primarily by molecular diffusion.

In some geologic settings, most of the groundwater flow occurs through fractures in rock formations that have very low permeabilities. The flow in the fractures often responds quickly to rainfall events and other fluid inputs, whereas the flow through the bulk matrix of the rock is extremely slow -- so slow that contaminant movement by molecular diffusion may be much quicker by comparison.

On the other end of the ground-water flow velocity spectrum is the flow in karst aquifers, since it may occur mostly through large channels and caverns. In these situations, groundwater flow is often turbulent, and the advection and dispersion of dissolved contaminants are not





contaminants are not adequately describable by Darcy's Law and other porous media concepts. Dye tracers have been used to study contaminant transport in fractured rock and karst aquifers, but such studies have yet to yield relationships (Figure 6) that can be transferred from the study site to other sites.



Regardless of the character of ground-water flow, contaminants may not be transported at the same rate as the water itself. Interruptions in contaminant movement occur as a result of sorption, ion-exchange, chemical precipitation, and biotransformation. The movement of a specific contaminant may be halted completely by precipitation or biotransformation, because these processes alter the chemical structure of the contaminant. Unfortunately, the resulting chemical structure may be more toxic and more mobile than the parent compound (Figure 7), such as in the case of anaerobic degradation of tetrachloroethene (PCE).

Figure 7 Biotransformation of PCE to TCE, DCE and Vinyl Chloride Biotransformation of PCE (suspected carcinogen, moderate retardation) may yield vinyl chloride (proven carcinogen, nearly water-coincident transport).

Sorption and ion-exchange (Figure 8), conversely, are completely reversible processes that release the contaminant unchanged after temporarily attracting it to a solid surface. This effect is commonly termed retardation and is quantified by projecting or measuring the mobility of the contaminant relative to the average flow velocity of the ground water. Projections of retardation effects on the mobility of contaminants are based on equations that incorporate physical (e.g., bulk density) and chemical (e.g., partition coefficients) attributes of the real system. Direct measurement of the effective mobility of contaminants can be made by observations of plume composition and spreading over time. Alternatively, samples of soils or sediments from the contamination site may be used in laboratory studies to determine the effective partitioning of contaminants between mobile (water) and immobile (solids) phases.



Figure 8 Retardation of Metals by Ion Exchange Metal ions carrying positive charges are attracted to negatively charged surfaces, where they may competatively replace existing ions.

Retardation effects can be short-circuited by facilitated transport, a term that refers to the combined effects of two or more discrete physical, chemical, or biological processes that act in concert to materially increase the transport of contaminants. Examples of facilitated transport include particle transport, cosolvation, and phase shifting.



Particle transport (Figure 9) involves the movement of colloidal particles to which contaminants have adhered by sorption, ion-exchange, or other means. Contaminants that otherwise exhibit moderate to extreme retardation may transport far greater distances than projected according to their nominal retardation values.

Pumping removes a great deal of colloidal particles, and much larger particles, from the subsurface (as witnessed by many well owners). This fact can complicate remediations, and is also relevant to public water supply concerns.

Figure 9 Contaminant Transport Facilitated by Colloidal Particles Sorption of organics (e.g., PCB's) or precipitation of metals (e.g., Pb) onto colloidal particles may be effective in increasing their transport.

Cosolvation is the process by which the solubility and mobility of a contaminant are increased by the presence of another contaminant, usually a solvent present at percent levels. Such phenomena are most likely to occur close to contamination sources, where the concentrations are typically highest. Treatment design strategies should thus anticipate the need to remove normally immobile organics from ground water that has been extracted in areas close to the source of contamination. Hcalth risk estimates, also, should factor in the increased mobility



Figure 10 Conceptualization of Facilitated Transport by Cosolvation Highly insoluble contaminants may dissolve in ground water containing an organic solvent, if the solvent is present at a high concentration (e.g., percent levels).

and exposure potential generated by cosolvation.



a large change in the pH or redox (reaction) potential of water, and can increase contaminant solubilities and mobilities by ionizing neutral compounds, reversing precipitation reactions, forming complexes with other chemical species, and limiting bacterial activity. Phase shifts may occur as the result of biological depletion of the dissolved oxygen normally present in ground water, or as the result of biological mediation of oxidationreduction reactions (e.g., oxidation of iron II to iron III). Phase shifts may also result from raw chemical releases to the subsurface.

Shifts between chemical phases (Figure 11) involve

Figure 11 Facilitated Transport by Phase Diagram Shifts (e.g. Iron) Releases of acidic contaminants, or depletion of oxygen by biota, may solubilize precipitated metals (e.g., iron). Neutral organic compounds also may ionize.

Some ground-water contaminants are components of immiscible solvents, which may be either floaters or sinkers (Figure 12). The floaters generally move along the upper surface of the saturated zone of the subsurface, although they may depress this surface locally, and the sinkers tend to move downward under the influence of gravity (Figure 13). Both kinds of immiscible fluids lcave residual portions trapped in pore spaces by wetting tension. This is particularly troublesome when an extraction well is utilized to control local gradients such that free product (the drainable gasoline) flows into its cone of depression; the



Figure 12 Immiscible and Miscible Contaminant Plumes Gasoline is an immiscible (insoluble) floater, whereas PCE is an immiscible sinker. Methanol is a totally miscible floater, whereas brines are highly miscible sinkers.

adversity is that the cone of depression will contain trapped residual gasoline below the water-table (Figure 14), which will become a continuous source of contamination, and which will persist even when the extraction well is turned off.



Reliable prediction of the future movement of contaminant plumes under natural flow conditions is difficult because of the need to evaluate properly the many processes that affect contaminant transport in a particular situation. Remediation evaluations are even more difficult because of extensive redirection of pre-remediation transport pathways by pump-and-treat wellfields. Hence, in terms of preparations for remediation, it is most important to determine the permeable pathways (where the ground water can go) during the site investigation.

Figure 13 Dynamics of Floater and Sinker Plumes Bouyant plumes migrate laterally on top of the water saturated zone. Dense plumes sink and follow bedrock slopes, which may oppose ground-water flow directions.



Figure 14 Zone of Contaminant Residuals Caused by Lamping Deep well pumping creates a cone of depression to trap gasoline for removal by skimmer pumps, but also creates a zone of contaminant residuals below the water table.

Design and Analysis Complications

There are serious unresolved questions about *how* one ought to evaluate the performance of pump-andtreat remediations. Neither contaminant distributions nor velocity distributions are constant throughout the *zone of action* (that portion of an aquifer actively manipulated by the pumping wells). Consequently, monitoring strategies must be cognizant of the need to detect rapid, sporadic changes in the quality of ground water at any specific point in the zone of action. This means that tracking the effectiveness of pump-and-treat remediations by chemical samplings is quite complicated. Decisions regarding the frequency and density of chemical samplings must consider the detailed flowpaths generated by the remediation wellfield, including changes in contaminant concentrations that result from variations in the influences of transport processes along those flowpaths. The need to reposition extraction wells occasionally, to remediate portions of the contaminated zone that were previously subject to slow flowlines, means that the chemical samplings may generate results that are not easily understood. It also means that it may be necessary to move the chemical compliance points during the course of a remediation.

Nor are evaluations of the hydrodynamic performance of remediation wellfields easily accomplished. For example, it is usually required that an inward hydraulic gradient be maintained at the periphery of a contaminant plume that is undergoing remediation by use of a pump-and-treat wellfield. This requirement is imposed to ensure that no portion of the plume is free to migrate away from the zone of action. To assess this performance adequately, the hydraulic gradient must be measured accurately in three dimensions between each pair of adjacent pumping or injection wells. The design of an array of *piezometers* (small diameter wells with very short screened intervals, that are used to measure the pressure head of selected positions in an aquifer) for this surface; but many more are needed to define the convoluted water-table surface that develops between adjacent pumping or injection wells. Not only are there velocity divides in the horizontal dimension near active wells, but in the vertical dimension, too, because the pressure influence of each well extends to only a limited depth in practical terms.

Limitations of Pump-and-Treat Remediations

Conventional remediations of ground-water contamination often involve continuous operation of an extraction-injection wellfield. In these remedial actions, the level of contamination measured at monitoring wells may be dramatically reduced in a moderate period of time, but low levels of contamination usually persist. In parallel, the contaminant load discharged by the extraction wellfield declines over time and gradually approaches a residual level in the latter stages (Figure 15). At that point, large volumes of water are being treated to remove small quantities of contaminants. Depending on the reserve of contaminants within the aquifer, this may cause a remediation to be continued indefinitely, or it may lead to premature cessation of the remediation and closure of



Figure 15 Apparent Clean-up by Pump-and-Treat Remediations Contaminant concentrations in pumped waters decline over time during pumpand-treat remediations, to an apparently irreducible level.

the site. The latter is particularly troublesome because an increase in the level of ground-water contamination may follow (Figure 16) if the remediation is discontinued prior to removal of all residual contaminants.



Figure 16 Contaminant Rebound After Pump-and-Treat Ceases Contaminant concentrations may rebound when pump-and-treat remediations cease, because of contaminant residuals.

There are several contaminant transport processes that are potentially responsible for the persistence of residual contamination and the kind of post-operational effect depicted in Figure 16. In order to generate such effects, releases of contaminant residuals must be slow relative to pumpage-induced water movement through the subsurface. Transport processes that generate this kind of behavior during continuous operation of a remediation wellfield include:

- diffusion of contaminants within spatially variable sediments,
- hydrodynamic isolation,
- sorption-desorption, and
- liquid-liquid partitioning.

1. Advection vs. Diffusion

Variations in rates of advection (flow velocity) that are caused by spatial variability of hydraulic conductivity result in rapid cleansing of higher permeability zones by extraction wellfields, because these sediments conduct virtually all of the flow. By contrast, it is only by the process of chemical diffusion that contaminants are removed from the low-permeability sediments, and the rate at which that occurs is dependent on the difference in contaminant concentrations within and external to the low permeability sediments (Figure 17). Hence, when the higher permeability sediments are cleaned up, the strength of chemical forces drawing contaminants from the lower permeability sediments is at its greatest and is exhausted only when the chemical



Figure 17 Variations in Permeability Limit Pump-and-Treat Effectiveness High permeability sediments conduct virtually all of the flow; low permeability sediments act as slowly leaking contaminant reservoirs.

when the chemical concentrations are nearly equal everywhere (or, at least, grade from greater to lesser such that no sharp differences exist). The orders-of- magnitude greater surface area of the low-permeability sediments allows significantly greater amounts of contaminants to accumulate on them during the pollution event/activity, in contrast to much lower accumulations of contaminants in high permeability sediments. The thicker the low permeability stratum, the more contaminant reserves it can hold, and the more diffusion controls contaminant movement overall. Hence, the majority of contaminant reserves may be available only under diffusion-controlled conditions in many heterogeneous settings. The situation is similar, though reversed, for in-situ remediations that require the injection and delivery of nutrients or reactants to the zone of intended action: access to contaminants in low permeability sediments is restricted to that provided by diffusion.

2. Hydrodynamic Isolation

The operation of any wellfield in a moving aquifer results in the formation of stagnation zones downgradient of extraction wells and upgradient of injection wells. The stagnation zones are hydrodynamically isolated from the remainder of the aquifer, so mass transport within the isolated water may occur only by diffusion. If remedial action wells are located within the bounds of a contaminant plume, such as for the removal of contaminant hot-spots, the portion of the plume lying within their associated stagnation zones will not be effectively remediated. The flowline pattern must be altered radically, by major changes in the locations of pumping wells, or by altering the balance of flowrates among the existing wells, or both, if the original stagnation zone(s) are to be remediated. Another form of hydrodynamic isolation is the physical creation of enlarged zones of residual hydrocarbon (Figure 14) that result when deep wells are used to create cones of drawdown into which underground storage tank and pipeline leaks of gasoline can flow, so that skimmer pumps can remove the accumulated product. When the deep water pump is turned off, the water table will rise to its pre-pumping position which will allow the rising aquifer waters that fill the cone of depression, and any subsequent groundwater flow through the former cone of depression, to become highly contaminated with BTEX compounds (e.g., benzene, the ethyl benzenes, toluene, and the xylenes) as a result of contact with the gasoline remaining on the aquifer solids (gasoline in residual saturation typically occupies from 20 to 40 percent of the pore space of the scdiments).

3. Sorption Influences

For sorbing compounds, the number of pore volumes to be removed depends not only on the sorptive tendencies of the contaminant but also on whether ground-water flow velocities during remediation are too rapid to allow contaminant levels to build up to equilibrium concentrations locally (Figure 18). If insufficient contact time is allowed, the affected water is advected away from sorbed contaminant residuals prior to reaching equilibrium and is replaced by fresh water from upgradient. Hence, continuous operation of pump-and-treat remediations results in steadystate releases of contaminants at concentration levels that may be substantially lower than their corresponding cquilibrium levels. With less contamination being removed per each volume of water brought into contact with the affected sediments, it is clear that large volumes of mildly contaminated water are recovered, where small volumes of highly contaminated water would otherwise be recovered.

Unfortunately, this is all too likely too occur with conventional pump-and-treat remediations (and with those in-situ remediations that depend upon injection wells for delivery of nutrients and reactants), because groundwater flow velocities within wellfields are many times greater than natural (non-



Figure 18 Sorption Limitations to Pump-and-Treat Effectiveness Increased flow velocities caused by pumpage may not allow ground-water contaminant concentrations sufficient time to reach maximum levels.

pumping) flow velocities, and increase exponentially with decreasing distance to the pumping locations. Hence, depending on the sorptive tendencies of the contaminant, the time to reach maximum equilibrium concentrations in the ground water may simply be too great compared with the average residence time in transit through the contaminated sediments.

4. Liquid-Liquid Partitioning



Again, this process generates large volumes of mildly contaminated water where small volumes of highly contaminated water would otherwise result, and this means that the remediation will pump and treat far more water than would otherwise be the case. The efficiency loss is



Figure 19 Liquid Partitioning Limitations of Pump-and-Treat Effectiveness Increased flow velocities caused by pumpage may not allow ground-water contaminant concentrations to reach maximum levels (same limitations as for sorption).

actually two-fold, because much of the pumped water will contain contaminant concentrations that are below the level at which optimal treatment is obtained.

Innovations in Pump-and-Treat Remediations

One of the promising innovations in pump-and-treat remediations is the idea of intermittent operation of a remediation wellfield, termed *pulsed pumping*. Pulsed operation of hydraulic systems is the cycling of extraction or injection wells on and off in *active* and *resting* phases (Figure 20). The resting phase of a pulsed-pumping operation can allow sufficient time for contaminants to diffuse out of low permeability zones and into adjacent high permeability zones, until maximum concentrations are achieved in the higher permeability zones; or, for sorbed contaminants and NAPL residuals, sufficient time can be allowed for equilibrium concentrations to be reached in local ground water. Subsequent to each resting phase, the active phase of the pulsed-pumping cycle removes the minimum volume of contaminated ground water, at the maximum possible concentrations, for the most efficient treatment. By occasionally cycling only select wells, their stagnation zones may be brought into active flowpaths and remediated.

Pulsed operation of remediation wellfields incurrs certain additional costs and concerns that must be compared with its advantages for site-specific applications. During the rest phase of pulsedpumping cycles, peripheral gradient control may be needed to ensure adequate hydrodynamic control of the plume. In an ideal situation, peripheral gradient control would be unnecessary. Such might be the case where there are no active wells, major streams, or other significant hydraulic stresses nearby to influence the contaminant plume while the remedial action wellfield is in the resting phase. The



Figure 20 Reduction of Residual Contaminant Mass by Pulsed Pumping Repeated removal of highly contaminated ground water pulses ensures effective depletion of contaminant residuals.

plume would migrate only a few feet during the tens to hundreds of hours that the system was at rest, and that movement would be rapidly recovered by the much higher flow velocities back toward the extraction wells during the active phase.

When significant hydraulic stresses are nearby, however, plume movement during the resting phase may be unacceptable. Irrigation or water-supply pumpage, for example, might cause plume movement on the order of several tens of feet per day. It might then be impossible to recover the lost portion of the plume when the active phase of the pulsed-pumping cycle commences. In such cases, peripheral gradient control during the resting phase would be essential. If adequate storage capacity is available, it may be possible to provide gradient control in the resting phase by injection of treated waters downgradient of the remediation wellfield. Regardless of the mechanics of the compensating actions, their capital and operating expenses must be added to those of the primary remediation wellfield to determine the complete cost.

Pump-and-treat remediations are underway today that incorporate some of the principles of pulsed pumping. For instance, pumpage from contaminated bedrock aquifers and other low permeability formations results in intermittent wellfield operations by default; the wells are pumped dry even at low flow rates. In such cases, the wells are operated on-demand with the help of fluid-level sensors that trigger the onset and cessation of pumpage. This simultaneously accomplishes the goal of pumping ground water only after it has reached chemical equilibrium, since equilibrium occurs on the same time frame as the fluid recharge event (both are diffusively restricted). In settings of moderate to high permeability, the onset and cessation of pumpage could be keyed to contaminant concentration levels in the pumped water, independent of flow changes required to maintain proper hydrodynamic/gradient control. As indicated in the discussion of pulsed pumping, this could be found to be acceptable (pose no unreasonable risk) in circumstances where the contaminant plume would not be subject to substantial movement in the absence of pumpage.

Other strategies for improvement of the performance of pump-and-treat remediations include:

- (1) flow scheduling of wellfield operations to satisfy simultaneously hydrodynamic/gradient control and contaminant concentration trends or other performance criteria,
- (2) physical repositioning of extraction wells to effect major flowline/transport pathway alterations, and
- (3) integration of wellfield operations with other subsurface technologies (e.g., barrier walls to limit plume transport and minimize pumping of fresh water; or, infiltration ponds to maintain saturated flow conditions for flushing contaminants from [normally] unsaturated soils and sediments).

The first of these by itself would allow for flushing of stagnant zones by occasionally turning off individual pumps, but the flushing could not be done as efficiently as when repositioning or addition of pumping wells is incorporated (the second means of improvement). The first and second approaches differ in effects, however, because repositioning or adding wells requires access for drilling -- necessarily precluding capping of the site until after completion of the pump-and-treat operations. The third improvement approach, combining pumpand-treat with subsurface barrier walls, trenching, or in-situ techniques (all of which may occur at any time during remediation), may also require postponement of capping until after completion of the remediation.

The latter raises latent fears of lack of control of the contaminant source, something almost always mitigated by isolation of the contaminated soils and subsoils that remain long after manmade containers have been removed from the typical site. Fortunately, vacuum extraction of contaminanted air/vapor from soils and subsoils has recently emerged a potentially effective means of removing VOC's (volatile organic carbon compounds), steam flooding is being evaluated for removal of the more retarded organics, and in-situ chemical fixation techniques are being tested for the isolation of metals wastes. Vacuum extraction has been shown to be capable of removing several pounds of VOC's per day (since the VOC's readily volatilize into the soil gas/vapor), whereas air stripping of VOC's from comparable volumes of contaminated ground water typically results in the removal of only a few grams of VOC's per day (because VOC's are so poorly soluble in water). Similarly, steam flooding has been shown to be an economically attractive means of concentrating contaminant residuals, as a front leading the injected body of steam. Regardless of the efficacy of vacuum extraction, steam flooding or chemical fixation in terms of permanent and complete remediation of the contamination in the unsaturated zone, they each have excellent potential for control of fluid and contaminant movement in the unsaturated zone, and should thus be considered as potentially significant additions to the list of source control options. In addition, soils engineering and landscape maintenance techniques can minimize infiltration of rainwater in the absence of a multilayer RCRA-style cap.

In terms of evaluation of the performance of a remediation, the presence of a multilayer RCRA-styled cap poses major limitations. The periodic removal of core samples of subsurface solids from the body of the plume and the source zone, with subsequent extraction of the chemical residues on the solids, is the only direct means of evaluating the true magnitude of the residuals and their depletion rate. Since this must be done periodically, capping would conflict unless postponed until closure of the site.

Hence, if capping can be postponed or forgone, great flexibility for management of pump-and-treat remediations can be had and used to improve effectiveness and lower costs. In so doing, another benefit accrues: the soils and suboils are cleansed of contamination, not simply waiting in isolation for eventual breakdown of a cap. Given the parallel theme of SARA -- true remediation, not just stabilized problems -- it is clear that innovative pump-and-treat remediations and source removal techniques may be the most economical and responsible choices for remediations henceforward.

Modeling as a Performance Evaluation Technique

Subsurface contaminant transport models incorporate a number of theoretical assumptions about the natural processes govening the transport and fate of contaminants. In order for solutions to be made tractable, simplifications are made in applications of theory to practical problems. A common simplification for wellfield simulations is to assume that all flow is horizontal, so that a two dimensional model can be applied, rather than a three-dimensional model (which is much more difficult to create and more expensive to use). Two-dimensional model representations are obviously not faithful to the true complexities of real world pump-and-treat remediations since most of these are in settings where three dimensional flow is the rule (e.g., water-table aquifers which change significantly in saturated thickness when pumped). Moreover, most pump-and-treat remediations utilize partially penetrating wells, which effect significant vertical flow components, whereas the two-dimensional models assume that the remediation wells are screened throughout the entire saturated thickness of the aquifer (and therefore do not cause upconing of deeper waters).

Besides the errors that stem from simplifying assumptions, applications of mathematical models to the evaluation of pumpand-treat remediations are also subject to considerable error in practical situations where the study site has been characterized inadequately. It is absolutely essential to have appropriate field determinations of natural process parameters and variables (Figure 21), because these determine the validity and usefulness of each modeling attempt. Errors arising from inadequate data are not addressed properly by mathematical tests such as sensitivity analyses or by the application of



Figure 21 Grid of Points Evaluated by a Contaminant Transport Model Known values of head (h), aquifer storage (S) and transmissivity (T), and other inputs are used to predict concentration (C) changes at each grid intersection (node).

stochastic techniques for estimating uncertainty, contrary to popular beliefs, because such tests and stochastic simulations assume that the underlying conceptual basis of the model is correct. One cannot properly change the conceptual basis (e.g., from an isolated aquifer to one that has strong interaction with a stream or another underlying aquifer) without data to justify the change. The high degree of hydrogeological, chemical, and microbiological complexity typically present in field situations forces one to seek site-specific characterization of the influences from various natural processes, by detailed field and laboratory investigations.

Hence, both the mathematics that describe models and the parameter inputs to those models must be subjected to rigorous quality control procedures. Otherwise, results from field applications of models are likely to be qualitatively, as well as quantitatively, incorect. It should be noted that these comments are particularly germane to pump-and-treat remediations, since the wide distribution of flow velocities (e.g., Figure 1) and the associated transport of contaminants along the flowlines generated within a remediation wellfield represent the most complex situations ever modeled in ground-water science. If done properly, however, mathematical modeling may be used to organize vast amounts of disparate data into a sensible framework that will provide realistic appraisals of which parts of a contaminant plume are being effectively cleansed, when the remediation will meet target contaminant reductions, and what to expect in terms of irreducible contaminant residuals. Models may also be used to evaluate changes in design or operation, so that the most effective (all portions of the contaminated zone impacted) and efficient (the least volume pumped /minimized total costs) pump-and-treat remediation can be attained.

The author is leading two research projects funded by EPA's Office of Research and Development, the *Remediation Performance* project at RSKERL/Ada and the *Pulsed Pumping* project at RREL/Cincinnati, that are well on the way to providing worked examples of the use of models for performance evaluations and improved remediation wellfield operations, respectively. Technical reports/publications are due from both projects by the end of FY89 (30 September 1989). When available, those reports will be used to update this document.

Other Data Analysis Methods for Performance Evaluations

Mathematical models are by no means the only methods available for use in evaluating the performance of pump-and-treat remediations. Two other major fields of analysis are statistical methods and graphical methods. The potential power of statistical methods has been tapped infrequently in ground-water contamination investigations, save for their limited use in quality assurance protocols. The worthwhile uses are many, however, as shown in Table 1.

Analysis of Variance (ANOVA) Techniques ANOVA techniques may be used to segregate errors due to chemical analyses from those errors that are due to sampling procedures and from the intrinsie variability of the contaminant concentrations at each sampling point. Correlation Constitution Correlation coefficients can be used to provide justification for lumping various chemicals together (e.g., total VOCs), or for using a single chemical as a class representative, or to link sources by similar chemical behavior. Regression Equations Regression equations may be used to predict contaminant loads based on historical records and supplemental data, and may be used to test cause-and-effect hypotheses about sources and contaminant release rates. Surface Trend Analysis Techniques Surface trend analysis techniques may be used to identify recurring and intermittent (e.g., seasonal) trends in contour maps of ground-water levels and contaminant distributions, which may be extrapolated to source locations or future plume trajectories.

Table 1. Statistical Methods Useful to Performance Evaluations of Remediations

Based on progress made thus far in the Remediation Performance project, it can be concluded that, while data interpretation and presentation methods vary widely, most site documents lack statistical evaluations and many tend to simplify datasets by inappropriate grouping or averaging of the data.

Graphical methods of data presentation and analysis have been utilized heavily in both ground-water flow problems (e.g., flowline plots and flownets) and water chemistry problems (e.g., Stiff kite diagrams, Piper trilinear diagrams, chemical distribution diagrams). Figure 1, for example is a flowline plot for a single well. From analysis of such plots, it is possible to estimate the number of pore volumes that will be removed over a set period of time of constant pumpage, at different locations in the contaminant plume. Figure 11 is a chemical phase diagram for iron, which may be used to relate pH and redox measurements to the most stable species of iron.



Figure 22 Pie-Chart Representation of Major Ions in a Ground-Water Sample The milli-equivalence values of each major ion are computed and plotted to generate easily identified patterns specific to the water source.



Figure 23 Stiff Diagrams of Major Ions in Two Water Samples The concentration of each ion is plotted in the manner shown in (a); the uniqueness of another sample is shown by (b). Figure 22 represents one means of producing readily recognizable patterns of the major ion composition of a water sample, so that it may be differentiated from other water types (such as natural background quality vs. contaminated waters). Similarly, Figure 23 represents another means of producing readily recognizable patterns of the milli-equivalence values of the major ions (related to their chemical reactivity) of a water sample. These graphical presentation techniques have been adapted recently to the display of organic chemical contaminants. For example, a compound of interest such as trichloroethene (TCE) may be evaluated in terms of its contribution to the total organic chemical contamination load, or against other specific contaminants, so that some differentiation of source contributions to the overall plume can be obtained.

Perspectives for Site Characterizations

Concepts pertinent to investigating and predicting the transport and fate of contaminants in the subsurface are evolving. An appreciation for this fact is important because there seems to be widespread overconfidence by decision makers regarding detection and remediation of contamination in the subsurface. From a practitioner's perspective, it appears that there is too little emphasis in most subsurface contamination assessments on obtaining detailed information about preferential pathways of contaminant transport and about the natural processes that affect the transport behavior and ultimate fate of contaminants. Additional effort devoted to site-specific characterizations of natural process parameters, rather than relying almost exclusively on chemical analyses of ground-water samples, may significantly improve the quality and cost-effectiveness of remedial actions at hazardous waste sites.

1. Characterization Approaches

To underscore the latter point, it is useful to examine the principal activities, benefits, and shortcomings of increasingly sophisticated levels of site characterization approaches: conventional (Table 2), state-of-the-art (Table 3), and state-of-the-science (Table 4). The conventional approach to site characterizations is typified by the description given in Table 2:

ACTIONS TYPICALLY TAKEN Install a few dozen shallow monitoring wells Sample ground-water numerous times for 129+ priority pullutants · Define geology primarily by driller's logs and drill cuttings · Evaluate local hydrology with water level contour maps of shallow wells · Possibly obtain soil and core samples for chemical analyses BENEFITS Rapid screening of the site problems * Costs of investigation are moderate to low Field and laboratory techniques used are standard * Data analysis/interpretation is straightforward * Tentative identification of remedial alternatives is possible SHORTCOMINCS * True extent of site problems may be misunderstood Selected remedial alternatives may not be appropriate · Optimization of final remediation design may not be possible Clean-up costs remain unpredictable, tend to excessive levels Verification of compliance is uncertain and difficult

Table 2. Conventional Approach to Site Characterization

Note that each activity of the Conventional Approach can be accomplished with semi-skilled labor and off-theshelf technology. Together with moderate to low costs, this ready availability of tools and techniques is reason enough for perpetuation of the Conventional Approach -- until one notes the shortcomings. It is not possible to thoroughly characterize the extent and probable behavior of a subsurface contaminant plume with the Conventional Approach; it is, by design, a compromise between the desire to discover the key problems at a site and the equal desire to keep expenses to an absolute minimum.

Key management uncertainties regarding the degree of health threat posed by a site, the selection of appropriate remedial action technologies, and the duration and effectiveness of the remediations all should decrease significantly with the implementation of more sophisticated site characterization approaches. Certainly, such has been the outcome in the several site investigations known to the author.



Table 3. State-of-the-Art Approach to Site Characterization

By inspection of Tables 2, 3, and 4, one may infer that it is likely to cost substantially more to implement state-ofthe-art and state-of-the-science approaches in site characterizations, but one should also infer that the increased value of the information obtained is likely to generate offsetting cost savings by way of dramatic improvements in the technical effectiveness and efficiency of the site clean-up.



Table 4. State-of-the-Science Approach to Site Characterization

These economic trade-offs are illustrated conceptually in Figure 24. The illustration provided there is meant to imply that modest increases in site characterization expenses (presumably for more sophisticated data collection and interpretation efforts) will generate large decreases in clean-up costs by virtue of greater effectiveness and efficiency of the remedial design and operation. In kind, total costs would fall dramatically with increased use of more sophisticated techniques, since clean-up costs normally comprise the majority of site expenditures.



Obviously, it is not possible to test these conceptual relationships directly, because one cannot carry an investigation and remediation to fruition along each approach simultaneously. The best that can be done is to note the magnitude of changes in perceptions, decisions, work plans, and the like, when more advanced techniques are brought to bear on a problem that has undergone a conventional level of site characterization. The latter situation is fairly common, because many first attempts at a remedial investigation turn up additional problems or complexities that were not suspected when the RI was budgeted and implemented, and because many first attempts at remedial investigations do not generate consistent or meaningful information.

Recognition that more technically sophisticated site characterization efforts are worthwhile is, of course, only the first step toward an improved remedy. Implementation of technically sophisticated site characterization approaches has been a widely lamented undertaking until recently, due to the scarcity of skilled labor and professionals knowledgeable in specialized techniques. Much has changed on that score in recent years, however, both demographically and legally. Demographically, it can be stated without reservation that there is rapid growth in the number of skilled professionals, as witnessed by the hundreds of training courses now offered apia growin in the number of skilled protestionaling, a transfer programs within EPA and other Federal and State agencies. Legally, the passage of the Superfund Amendments and Reauthorization Act (SARA) gave EPA and interested parties the opportunity to test promising technologies at Superfund sites.

Incorporation of some of the more common state-of-the-art site investigation techniques, such as pump tests, installation of vertically-separated clusters of monitoring wells (shallow, intermediate, and deep) and river stage monitors, and chemical analysis of sediment and soil samples would likely result in the kind of remediation illustrated in Figure 27. Since a detailed understanding of the geology and hydrology would be obtained, optimal selection of well locations, wellscreen positions and flowrates (the values in parentheses, in gallons per minute) for the remediation wells could be determined. A special program to recover the acid plume and neutralize it would be instituted. A special program could also be instituted for the pesticide plume. This approach would probably lower treatment costs overall, despite the need for separate treatment trains for the different plumes, because substantially lesser amounts of ground-water would be treated with expensive carbon filtration to remove non-volative contaminants.



Figure 27 Moderate State-of-the-Art Clean-up of the Hypthetical Ground-Water Contamination Site Clusters of vertically-separated monitoring wells and an aquifer test are used to tailor the remedy to the hydrogeology of the site.

The extraction wellscreens positions become increasingly deeper as one gets closer to the river, because monitoring well clusters have indicated that the plume is migrating beneath shallow accumulations of clays and silts to the deeper, more permeable sediments. Approximately two-thirds of the extracted and treated ground water is reinjected through injection wellscreens that have been positioned deep to avoid diminishing the effectiveness of nearby extraction wells. As in the conventionally-based remedy, the remediation wellfield would be scheduled to operate for the amount of time needed to remove a volume of water that is based on average contaminant retardation values and the volume of ground water residing in the zone of contamination -- except that the detailed geologic and hydrologic information acquired would result in an expectation of more rapid cleansing of specific portions of the zone of contamination than elsewhere. The decision makers would have based their approval of this remedy on the presumption that the remediation is optimized to the point of providing the most effective clean-up, though the efficiency of the remediation may be less than optimal. If all state-of-the-art investigation tools were used at the site, there would be an opportunity to evaluate the desirability of using a subsurface barrier wall to enhance remediation efforts (Figure 28). The wall would not be expected to entomb the plumes, but would serve the purpose of limiting pumping to contaminated fluids; rather than having the extracted waters diluted with fresh waters available to the extraction wells, as was true of the two previous approaches. The volume pumped would be lowered because the barrier wall would increase the drawdown at each well by hydraulic interference effects, thereby maintaining the same effective hydrodynamic control with lesser pumpage (note the lower values in parenthesis, at each well). Treatment costs would be lowered as well, because the waters pumped would contain higher concentrations of contaminants; treatment efficiencies normally fall with decreasing concentrations. Soil washing techniques would be used on the pesticide contaminated area to minimize future source releases to ground water.



Figure 28 Advanced State-of-the-Art Clean-up of the Hypothetical Ground-Water Contamination Site Subsurface barrier walls or other technologies can be integrated with pump-and-treat operations for improved effectiveness and efficiency.

The efficiency of the remediation would therefore appear to be optimal, as well as the effectiveness, but that is a perception based on the presumption that contaminants are readily released. Given the potential limitations to pump-and-treat remediations that were discussed in earlier sections of this document, however, it is doubtful that this advanced state-of-the-art site investigation precludes further improvement. Just as much attention to the chemical and biological pecularities is needed, as has been given to the geology and the hydrology. The use of average retardation values from the literature infers that additional improvements in effectiveness and efficiency can be garnered by detailed evaluation of contaminant retardation at this site. Likewise, detailed examination of the potential for biotransformation would be expected to garner additional effectiveness and efficiency. At the state-of-the-science level of site characterization, tracer tests could be undertaken which would provide good information on the potential for diffusive restrictions in low permeability sediments and on anisotropic biases in the flow regime. Sorption behavior of the VOC's could be evaluated in part by determinations of the total organic carbon contents of the subsurface sediments. Similarly, the cation exchange capacities of subsurface sediment samples could be determined to obtain estimates regarding release rates and mobilities of toxic metals. The stabilities of various possible forms of elements and compounds could be evaluated with measurements of pH, redox potential, and dissolved oxygen -- something that may be particularly germane to the acids plume and the phenols plume. Finally, if state-of-the-science findings regarding potential biotransformations could be taken advantage of, it might be possible to effect in-situ degradation of the phenols plume, and remove volatile residues too (Figure 29).



Figure 29 State-of-the-Science Clean-up of the Hypothetical Ground-Water Contamination Site Bioreclamation and other emerging technologies could be tested and implemented with reasonable certainty about the outcome.

The foregoing discussion should serve to signify the tremendous gains in effectiveness and efficiency of remediation that should be expected by better defining ground-water contamination problems and using that information to develop site-specific solutions, rather than implementing generalized solutions that have come into common practice out of a lack of recognition of the true economics involved. Moreover, it is only by a thorough understanding of the problem, generated during the site characterization studies, that one is afforded the opportunity to evaluate the performance of a pump-and-treat remediation. It is essential that such evaluations be conducted, because pump-and-treat is not a proven technology. Rather, pump-and-treat remediation is a method of fluid removal borrowed from water-supply technology, where an adequate supply of ground water -- not management of water quality variations -- has been the primary objective.

Summary/Conclusions

Pump-and-treat remediations are far more complicated than previously thought. The variations in groundwater flow velocities and directions that are imposed on natural systems by remediation wellfields tremendously complicate attempts to evaluate the progress of pump-and-treat remediations, in part because of the tortuosity of the flowlines that are generated, and in part because historical trends of contaminant concentrations at monitoring wells are rendered useless for further predictions and evaluations. Just as it is improbable that a proper understanding of the true extent of the contamination problem can be obtained unless sophisticated site characterization approaches are utilized, it is not possible to optimize the effectiveness and efficiency of a pumpand-treat remediation unless the geologic, hydrologic, chemical, and biological complexities of a site are defined adequately. While it is evident that no gaurentee can be given that a remediation will indeed be completely effective and optimally efficient by virtue of the use of state-of-the-art and state-of-the-science techniques, it is equally evident that their use ensures the best that can be achieved practically.

Acknowledgements

This document is the primary product of Phase 1 of the Remediation Performance project, sponsored by the U.S. Environmental Protection Agency. The assistance of Ms. Julie Valenter in preparing the illustrations is greatly appreciated. Review comments by members of EPA's Robert S. Kerr Environmental Research Laboratory were invaluable in revising previous drafts. The author assumes responsibility for all errors and welcomes comments by the reader.

Optimizing Pumping Strategies for Contaminant Studies and Remedial Actions

by Joseph F. Keely

Abstract

One of the more common techniques for controlling the migration of contaminant plumes is the use of pumping wells to produce desired changes in local flow rates and hydraulic gradients. When seeking to optimize an array of pumping well locations and discharge rates, it is important to consider the effects that non-ideal aquifer conditions, well construction and demographic constraints produce. Heterogeneous and anisotropic aquifer conditions seriously complicate siting and discharge rate requirements for pumping wells because of the distorted cones of depression that result from withdrawing water in such settings. Proper screen selection, gravel pack emplacement and well development are crucial factors affecting the operational characteristics and economics of pumping wells; these factors are generally recognized, though often undervalued. The impacts that well depth and diameter, and screen length and position have on the effectiveness of pumping efforts are also often undervalued, with detrimental consequences. Perhaps the most difficult problems to overcome in designing pumping schemes, however, are posed by demographic constraints. Denial of property access, vandalism and the unpredictability of nearby water supply and irrigation pumpage tend to wreak havoc with the best of pumping strategies.

Introduction

Safe storage and disposal of hazardous wastes have become major social issues because of the discovery that many sites lack proper precautions for the prevention of soil and water contamination. Ground water contamination has received the major share of society's attention to these issues, primarily because the route of human exposure by this pathway is direct. In practical terms, this means that the level of cleanup of the damage done by contamination incidents is often dictated by social concerns (e.g. health risk). Plume stabilization by interception and control with perimeter wells, injection and recovery loops, and other pumping schemes may be chosen as the "remedial action" appropriate for a particular plume. The affected plume may be held in place and treated, it may be held and allowed to move on after alternate public supplies have been located for downgradient water systems, it may be held in place to allow biodegradation of particular constituents, or it may be held until better treatment procedures can be devised.

Factors Affecting Pumping Strategies

Hydrodynamic control and recovery strategies vary considerably in their efficiencies. Besides the obvious need to choose the well locations and flow rates carefully, a number of other considerations demand attention (Figure 1). Non-ideal aquifer conditions are a reality for virtually all real-life situations; heterogeneity is the rule rather than the exception. Three-dimensional anisotropy, as expresed by the vertical vs. horizontal hydraulic conductivity ratio, is a near certainty for most strata. Less visibly pronounced, yet almost as prevalent, is an expressed anisotropy in the horizontal plane of many strata. These commonplace non-ideal aquifer conditions complicate our perception of where a given plume can go (Fetter 1981) under both natural flow conditions and remedial action pumping schemes. The preferential flow paths that are created by buried lake beds, glacial outwash gravels, streambeds, coastal deposits and the like cannot be delineated without expensive and time-consuming field tests. Likewise, it is nearly impossible to accurately predict the magnitudes of distortion in the cones of depression created by wells pumping from heterogeneous, anisotropic aquifers.

Variations in the properties of the fluid in an aquifer, particularly the solution density, also can significantly affect the behavior of contaminant plumes (Jorgenson et al. 1982). Immiscible plumes with lower density than that of the native ground water will float at the surface of the saturated zone, traveling along the same general gradient, but traveling at a different rate than the underlying ground water. Immiscible plumes with greater density than that of the native ground water will sink through the ground water. losing small but significant amounts of low solubility constituents as they move. Miscible plumes of any density, by definition, mix intimately with native ground water. The duration of time required to achieve a specific dilution by this mixing changes markedly, however, and is generally inversely related to the density. For most situations, the greater the density, the shorter the mixing period. The exception to this general rule would be the case of a large volume of highly dense, miscible fluid penetrating a shallow aquifer quickly enough to reach bedrock in a relatively undisturbed form.

Considerations

Non-Ideal Aquifer Conditions:

- Heterogeneity
- Anisotropism
- Variable density

Well Construction Effects:

- Partial penetration
- Partial screening
- Incomplete development

Anthropogenic Influences:

- Property access
- Vandalism
- Unknown pumpage/injection

Other Factors:

- Physiochemical attenuation
- Biological transformations
- Operational failures

Figure 1. General considerations for optimizing pumping strategies

These complexities work against us if we are ignorant of them. Working up an appropriate recovery system for a contaminant plume can be compared to designing an oil production system. What you get out depends directly on what you put in-up to a point. Where that break-even point comes is hard to say. given unknowns like the source strength and timing. and immeasurables like the dollar value of additional cancer victims. What is abundantly clear, however, is that there is a substantial minimum for serious play. One does not blithely draw up plans to pump and treat a plume until considerable manpower and funds are expended to obtain information on the natural flow direction, gradient and velocity. The question is usually one of how much to spend to reach some desired level of detail: the level of detail is set by social concerns.

This seems to be logical application of technology for social need, but the logic may be shortsighted. If social concerns (based on preliminary evaluation of a contaminant incident) are minimal, there is no guarantee that such social concerns are appropriate. Additional studies, which could delineate preferential flow paths and quantify factors affecting contaminant behavior, might well generate findings that would justify considerably greater or lesser social concern. Quite often data from preliminary investigations are limited to samples from shallow on-site wells, which may fail to signify the potential impact of dense plumes or seasonally-occurring leachate plumes that have moved off-site. Additionally, the preliminary investigation wells are not normally installed to a sufficient depth for appreciation of the local stratigraphic and lithologic characteristics of the aquifer.

In addition to a better understanding of where contaminants might go with the natural flow, a second powerful argument to avoid "penny-wise and poundfoolish" investigations concerns the need to provide the best information possible for targeting well locations and pumping strengths in remedial actions. The occurrence of specific heterogeneities can be used to advantage by locating wells near low permeability clay units to generate greater drawdown for a given pumping rate. Likewise, knowledge of the direction of the principal horizontal axis in anisotropic strata can help to maximize the arrangement of the "troughs of depression" for wells to be located in such settings: knowledge of the magnitude of vertical anisotropy can help determine the amount of water pumped from strata containing contaminants vs. the amount of "clean" water from the other strata open to the well.

This latter factor. vertical anisotropy, leads to examination of some of the more controllable items to be considered in optimizing pumping strategies—well construction effects. For example, the impact that partial penetration of a fully screened pumping well can have on the estimate of potential for contamination of a water supply or on the effectiveness of a remedial action scheme is tremendous (Saines 1981). The effect is to cause exaggerated drawdowns near the well. The magnitude of the effect is inversely dependent on the degree of penetration of the well into the aquifer, being greatest for slight penetration. Naturally, partial screening of a fully penetrating well results in the same effect—greater drawdown for a given pumping rate as compared with a fully screened, fully penetrating well.

Again, knowledge of these factors can be used to enhance a pumping scheme that is, for example, designed to maintain hydrodynamic control of a plume at the lowest possible level of pumpage. Lack of appreciation of these well construction effects can result in poor estimates of potential contaminant impacts on supply wells and in poorly designed remedial action schemes. Another effect worthy of mention is that generated by well development practices. If a well is properly developed, the drawdown measurable inside the well will agree with the level projected by close observation wells. More often, however, a well is not perfectly efficient because the well development procedures were not adequate to remove drilling fluid fines and locally disturbed aquifer material resulting from the drilling process. These materials lower the permeability of the gravel pack and formation immediately adjacent to the well. The greater the degree of well inefficiency caused by lack of proper development, the greater the amount of non-productive drawdown inside the well; this means that the well may never be able to pump at design capacity without risk of running dry. and it means increased operating expense due to the additional pump lift required. What it may also portend, for seriously inefficient wells, is that certain strata penetrated by the well may be effectively sealed by drilling mud or by natural clays that were smeared over the borehole face by the actions of the drilling operation. Such "sealed off" strata may carry the bulk of the contaminants, resulting in poor recovery of the plume.

Some of the most significant, though less controllable, factors that should be considered when optimizing pumping strategies concern direct anthropogenic influences: denial of property access. vandalism and unknown pumpage all tend to wreak havoc with the best laid plans. Bedient et al. (1984) describe efforts to delineate a plume of contaminants migrating under a residential area from an abandoned wood creosoting plant in Conroe. Texas:

"Several wells exist in the general flow direction, but not directly downgradient from the waste pit locations. Access was not granted for installing monitoring wells...Approximately 50 percent of the chloride plume has been defined since the monitoring well network is incomplete at this time...Completion of the monitoring well network is needed to capture the center of the contaminant plume. This will require more wells downgradient on land that has not previously been accessible for investigation."

The granting of property access during investigations of ground water contamination incidents in populated areas is no trivial matter. One typically finds it necessary to contact not only homeowners and landlords for private property access, but also to negotiate with company engineers, vice presidents and attorneys for commercial property access. It is quite normal for such negotiations to be involved and protracted as city councils, educational boards, corporate headquarters and other bureaucratic entities are asked to concur in signing access agreements containing provisions deemed necessary to ensure against incurred liability and potential damage.

The role played by unknown pumping and/or injection wells operating near a remedial action pumping system is subtle but far-reaching. Such unknown stresses can significantly distort the flow field and render remedial actions ineffective. Projections on plume movement made during an investigation of a ground water contamination incident would also be in error if unknown wells are causing distortion in the flow field; both the direction and the speed of the plume could be dramatically altered. The reason for the subtlety of the effects of many such wells is that their cyclic, seasonal or on-demand pumping schedules allow them to be detected only by continuous recording of water level changes at numerous points around the zone of interest. Since aquifer responses at a given observation point are somewhat non-unique. merely detecting extraneous sources of drawdown does not automatically result in identification of the sources.

There are a few other important factors to consider that also affect pumping strategies. The physiochemical properties of the contaminant itself can result in a need to pump several pore volumes from each unit volume of aquifer to be decontaminated. Sorption, ion exchange and speciation changes can result in retarded movement of contaminants relative to the average velocity of the water with which they are initially associated. Biotransformation of contaminants may result in reaction products (daughter products) that are of greater or lesser toxicity, mobility and persistence-in other words, uncertain contaminant behavior. Unlike the aquifer properties of storage coefficient, saturated thickness and hydraulic conductivity, which can be readily determined, the current state-of-the-science with regard to determining the potentials for physiochemical attenuation and biotransformation is not up to the level of routinely providing reliable answers on a site-specific basis.

Finally, an obvious but often overlooked consideration involved in optimizing pumping strategies is the need to develop adequate contingencies for operational failures. This means some intentional overdesign for reserve capacity, total redundancy of key wells and electronic controls, backup power systems and so on. It also means bonding or insurance against unforeseen catastrophies so that as little downtime is expended as possible. It may also mean that an escrow account or trust fund must be established to provide the necessary capital for replacement of burned-out or inadequate pumps, deepening or abandonment of existing wells, or drilling of additional wells.

Capture Zones vs. Zones of Pressure Influences

Keely and Tsang (1983) introduced the term "capture zone" to describe that portion of the aquifer affected by pumping which actually yields water to the well. They have shown that the capture zone is generally much smaller than the zone of pressure influence because a balance is achieved, under steady-state conditions, between the pull of water back toward the well from its downgradient side and the tendency of the natural flow system to move on further downgradient. Figure 2 is a series of four idealized illustrations that present conceptualizations of how the size of the capture zone changes, relative to the zone of pressure influence/cone of depression, as the local gradient

is increased. In Figure 2A the well is pumping from a stagnant aquifer, indicated by the flat pre-pumping surface, overlaid on the theoretical cone of depression that would occur during pumpage. For stagnant aquifer conditions, the capture zone is everywhere identical to the zone of pressure influence and flow is radial into the well. As the successive diagrams indicate, however, non-stagnant aquifer conditions lead to smaller capture zones (Figures 2B to 2D).

The slopes of the pre-pumping surfaces are overlaid on the theoretical drawdown cones in each frame of Figure 2 to emphasize the interaction of the natural flow system with the pumping stress to yield a capture zone smaller than the zone of pressure influence. There is no intention to show the net surface resulting from pumpage by subtracting theoretical drawdown values from pre-pumping water elevations. These sketches do have the cosmetic drawback of showing crossing water level lines/curves, but the point is to illustrate the individual components of the net surface (crosssectional view) and how they interact to yield a capture zone (three-dimensional view).

The flow lines generated by pumping a well from an idealized aquifer (homogeneous, isotropic, constant density. etc.) under different natural flow conditions are shown in Figure 3. In Figure 3 a well pumping 1.000m³/day from a 10m thick aquifer having a porosity of 0.10 and a hydraulic conductivity of 100m/day has uniform radial flow under stagnant aquifer conditions (e.g. natural flow velocity equal to zero). When a mild hydraulic gradient (0.0001) is imposed on the same system (Figure 3B), the resulting natural flow velocity (0.1 m/day) is insufficient to significantly affect the flow lines, and uniform radial flow is nearly maintained. With a more moderate hydraulic gradient (0.001), the resulting natural flow velocity (1.0m/day) is sufficient to sweep away many of the flow lines and the capture zone is clearly evident (Figure 3C). Where a steep gradient (0.01) is present, the capture zone diminishes to a small fraction of the zone of pressure







Figure 3. Flow line plots for a single well discharging 1,000m³/day from an aquifer with 10m saturated thickness, 100m/day hydraulic conductivity and 0.10 porosity

NOTE: Scale is in meters and natural flow proceeds from lower left-hand corner to upper right-hand corner of each plot at the velocity indicated.

influence (Figure 3D).

Comparing Pumping Strategies

A typical use of pumping schemes is to effect hydrodynamic control over a plume, either for longterm stabilization or for withdrawal and treatment. Consider extending the example illustrated by Figure 3. First, assume a line of five wells lying perpendicular to the direction of natural flow (Figure 4). Each of the five wells pumps 200m³/day, so that the total pumpage of the five wells is the same as that of the single well in Figure 3. Under stagnant aquifer conditions to low natural flow velocities (Figures 4A and 4B) there does not seem to be any difference in the effectiveness of the pumpage from the five wells as compared with the single well case (Figures 3A and 3B). The situation changes markedly if moderate to high natural flow velocities are present, however, as depicted in Figures 4C and 4D. As the natural flow velocity increases, the capture zone of each of the five wells diminishes to a point where adjacent capture zones no longer overlap and natural flow lines run on through the line of wells. By contrast, the capture zone of the single well pumping 1.000m³/day does not develop holes, but does diminish in size to well below the perceived size of the leaky collective capture zone of the line of five wells.

In actuality, there is no difference between the true collective size of the capture zones generated by the five wells and that generated by the single, high-flow





NOTE: Scale is in motors and natural flow proceeds from lower left-hand corner to upper right-hand corner of each plot at the velocity indicated.

rate well. By rearranging some of the expressions for capture zone dimensions given by Keely and Tsang (1983), it is possible to define the maximum width of the capture zone upgradient of the well as: $W_{max} = \bigcirc +$ $(h\phi_e V_{nat})$. Using this relationship, it is apparent that the maximum width (W_{max}) of the capture zone of a well is directly and linearly related to its flow rate (\bigcirc), and is inversely related to the natural flow velocity

(V_{nal}). For the example discussed here regarding a single well pumping 1,000m³/day, the maximum width of the capture zone is 1,000m when the natural flow velocity is 1.0m/day, and is 100m when the natural flow velocity is 10m/day. Each of the flve wells in the second example discussed pumps at a flow rate equal to one-fifth the flow rate of the well in the first example (200m³/day), and each, therefore, has a capture zone the maximum width of which is one-fifth that of the single well (200m). Hence, by comparing Figure 3 with Figure 4, it is seen that the way in which the total pumpage is distributed does directly affect the distribution of the capture zone(s), but does not affect the magnitude or total area of the capture zone(s). Also to be seen in Figures 3 and 4 is that increasing the natural flow velocity estimate can have a dramatic impact on the effectiveness of the pumping strategy. Given the order-of-magnitude uncertainty so often associated with hydraulic conductivity estimates, it is not surprising that many seemingly acceptable remedial action schemes are doomed to fail miserably.

A more complicated example provides further illustration of these points. Assume that we have the same





NOTE: Scale is in meters and natural flow proceeds from lower left-hand corner to upper right-hand corner of each plot at the velocity indicated.

aquifer conditions and total pumpage limitation $(1.000m^3/day)$ as the preceding examples. We will distribute the pumpage uniformity by pumping each of eight wells at $125m^3/day$. The eight wells are evenly spaced around a circle of 200m radius. We are trying to hold a plume within the circle. With stagnant aquifer conditions to low natural flow velocities, the plume appears to be stable; no flow lines pass through the circle (Figures 5A and 5B). At moderate to high natural flow velocities, however, the situation is quite different; flow lines readily pass through the circle, indicating that the plume stabilization attempt has failed (Figures 5C and 5D).

A pump and treat scenario can be examined by modifying the example shown in Figure 5 to change the operation of the eight wells from pumping to injecting and by adding a major pumping well in the center of the circle. The single pumping well will withdraw 1.000m³/day from the plume. The withdrawn water will be treated and re-injected into the eight injections wells at 125m³/day each. At zero to low flow velocities, the injected water flows radially toward the central pumping well, forming a closed loop for recoverv and treatment of the plume (Figures 6A and 6B). At moderate to high natural flow velocities, the recovery loop is broken and an increasing amount of the injected water and the plume are swept away by the regional flow (Figures 6C and 6D). It must be emphasized that the cones of impression or depression of the wells overlap significantly for all of the multiwell examples discussed so far. Despite those overlaps, the net surface resulting from the natural gradient and the













Figure 6D. Steep hydraulic gradient (0.01)

Figure 6. Flow line plots for a single well discharging 1,000m³/day, encircled by eight wells injecting 125m³/ day into an aquifer with 10m saturated thickness, 100m/day hydraulic conductivity and 0.10 porosity

NOTE: Scale is in meters and natural flow proceeds from lower left-hand corner to upper right-hand corner of each plot at the velocity indicated.

water level changes due to pumpage and/or injection is shaped such that the streamilnes are truly as presented here. For further discussion of capture zones and velocity distribution plots, see Keely and Tsang (1983). The detailed theoretical development and source code listings for the models that were used to generate the stream line plots shown here are given in Javandel et al. (1984).

A Little More Detail

It was quite clear in each of the preceding examples that the pumping strategy began to fail as the natural flow velocities became appreciable. The tendency to fail is generally becoming evident at a natural flow velocity of 1.0m/day and is beyond question at a natural flow velocity of 10m/day. Figure 7 shows that failure of each design is certain at 5.0m/day as well: the point at which the flow lines break through must be at much lower natural flow velocities.

In Figure 8 the natural flow velocity has been reduced to 0.5 and 0.4m/day for the last two examples only. Breakthrough of the streamlines (failure of the pumping strategy) occurs somewhere between the 0.4 and 0.5m/day natural flow velocities. Similar comparisons for the first two examples are not presented because flow line breakthrough does not apply to the first example (a single production well) and the flow line did not indicate breakthrough at 1.0m/day for the second example (a line of five wells).

The presence of an unknown well is being studied in Figure 9. A major pumping well (1.000m³/day) has been arbitrarily located downgradient of the same line







Figure 7B. Line of five wells, each discharging 200m³/day



125m³/day

by eight wells injecting 125m³/day each.

Figure 7. Comparison of pumping arrays in an aquifer with 10m saturated thickness, 100m/day hydraulic conductivity, 0.10 porosity and 0.005 hydraulic gradient

NOTE: Scale is in meters and natural flow proceeds from lower left-hand corner to upper right-hand corner of each plot at the velocity indicated.

of five wells discussed in the second example. Naturally. under stagnant aquifer conditions, the unknown well creates a hydraulic divide by distorting the flow field. but it does not cause breakthrough of the flow line from across the line of five wells (Figure 9A). With a natural flow velocity of 0.5m/day, however, flow lines do begin to break through the line of five pumping wells (Figure 9B). Substantial failure of the pumping scheme occurs at 1.0m/day natural flow velocity (Figure 9C). Contrast the onset of breakthrough due to unknown pumpage (Figure 9B) with the same situation in the absence of the unknown pumpage (Figure 9D). The impact of the unknown well is staggering, not only because flow line breakthroughs are occurring, but the collective size of the capture zones of the five pumping wells is being substantially reduced.

Another illustration of the impact of an unknown well on the effectiveness of a pumping scheme is shown in Figure 10, which is the same example as discussed earlier (Figure 6) for a closed-loop aquifer rehabilitation system. Under stagnant aquifer conditions, the unknown well diverts flow away from two of the injection wells (Figure 10A). At 1.0m/day natural flow velocity, the unknown well diverts flow from five of the eight injection wells (Figure 10B). It also allows flow to break away from the well field entirely. as indicated by the streamline leaving the uppermost injection well and heading downgradient in Figure 10B. The regional flow lines were omitted from Figure 10 and some of the diagrams in previous figures because inclusion of those flow lines would create confusion due to the excessive number of plotted points.





Figure 8A. Circle of eight wells, each discharging 125m³/day with 0.0004 hydraulic gradient







Figure 6C. Single well discharging 1,000m³/day, encircled by eight wells injecting 125m³/day each, with 0.0004 hydraulic gradient Figure 8D. Single well discharging 1,000m³/day, encircled by eight wells injecting 125m³/day each, with 0,0005 hydraulic gradient

Figure 8. Detailed views of the onset of flow line breakthroughs for two plume control strategies in an aquifer with 10m saturated thickness, 100m/day hydraulic conductivity and 0.10 porosity

NOTE: Scale is in meters and natural flow proceeds from lower left-hand corner to upper right-hand corner of each plot at the velocity indicated.

Conclusions

Heterogeneity, anisotropy, partial penetration and so on distort drawdown patterns and associated velocity distributions. If known, such influences can be used to enhance recovery efficiencies for remedial actions. If unknown, such influences may cause recovery efficiencies to be substantially lowered. Similarly, predictions of plume migration in non-ideal aquifers under non-pumping/natural flow conditions will be strengthened by specific knowledge regarding the occurrences. extent and magnitude of the non-ideal condition(s). Such predictions may be seriously in error if non-ideal conditions are not evaluated properly.

Denial of property access, loss by vandalism and

unpredictable operation of nearby wells are also major sources of uncertainty in predicting contaminant migration and in designing remedial actions. Though commonly perceived to be less of an impact on optimizing pumping strategies than non-ideal aquifer conditions, these factors may indeed be the most uncontrollable and the most detrimental to operational success. Other factors that have major impacts are the physiochemical attenuation and biotransformation potentials of the individual contaminant; it is not yet aconomically feasible to conduct adequately detailed studies of these potentials on a routine sitespecific basis. Finally, a factor often overlooked that greatly impacts optimization efforts is the risk of



Figure 9. Influence of an unknown well discharging 1,000m³/day on flow line breakthroughs for a line of tive wells discharging 200m³/day each from an aquifer with 10m saturated thickness, 100m/day hydraulic conductivity and 0.10 porosity

NOTE: Scale is in meters and natural flow proceeds from lower left-hand corner to upper right-hand corner of each plot at the velocity indicated.

mechanical and electrical operational failure: adequate contingency plans must provide certain minimal levels of excess/reserve capacity and redundancy of key system components.

The capture zones of wells do not equal their associated zones of pressure influence (cones of depression), except for stagnant aquifer conditions. Velocity distribution plots must be constructed to define potentials of contaminant migration. in particular, plotting the streamlines for various scenarios involving pumping and/or injection wells subject to a specific natural flow velocity can greatly assist the ground water professional in selection of an optimal pumping strategy.

Acknowledgments

Thanks go to Rosemary Keely and Christine Doughty for (computer) drafting the illustrations. Thanks also go to Renae Daniels for typing this manuscript.

Disclaimer

Although this article was produced by an employee of the United States Environmental Protection Agency. it has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency: no official endorsement should be inferred.



Figure 10. Influence of an unknown well discharging 1,000m³/day on flowline breakthroughs for a single well discharging 1,000m³/day that is encircled by eight wells injecting 125m³/day into an aquifer with 10m saturated thickness, 100m/day hydraulic conductivity and 0.10 porosity.

NOTE: Scale is in meters and natural flow proceeds from lower left-hand corner to upper right-hand corner of each plot at the velocity indicated.

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Biographical Sketch

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APPENDIX F

SUPPLEMENTARY MATERIAL FOR IN-SITU SOIL WASHING AND FLUSHING TECHNOLOGIES Thomas C. Sale, CH2M Hill, Denver, Colorado

EPA/600/2-87/110 December 1987

2000-140000

FIELD STUDIES OF IN SITU SOIL WASHING

by

James H. Nash Mason & Hanger-Siles Mason Co., Inc. P.O. Box 117 Leonardo, New Jersey C7737

Contract No. 68-03-3203

Project Officer

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Richard P. Traver P.E. Releases Control Branch Land Pollution Control Division Edison, New Jersey 08837

HAZARDOUS WASTE ENGINEERING RESEARCH LABORATORY OFFICE OF RESEARCH AND DEVELOPMENT U.S. ENVIRONMENTAL PROTECTION AGENCY CINCINNATI, OHIO 45268
ABSTRACT

The U.S. Environmental Protection Agency Releases Control Branch and the U.S. Air Force Engineering and Services Center engaged in a joint project focused on <u>in situ</u> washing of a fire training pit at Volk Air National Guard (ANG) Base, Camp Douglas, Wisconsin. The washing fluids were solutions of commercially available surfactants in water. Of particular interest was a blend of Adsee 799 and Hyonic PE90. This blend had previously proved successful in laboratory studies involving the cleaning of organic contaminants from soll. A second objective was to treat contaminated groundwater underlying the test site.

The fire training pit had served as a site for firefighting training as early as World War II up until deactivation in 1979. The subsurface soil was determined to be 85-95% sand and 5-15% fines. The contamination was principally a medium weight oil (2,000-25,000 mg/kg) with some volatiles (VOA analysis 5-10 mg/kg). The unconfined anulfer at 12 feet depth is reported to be continuous to 700 feet. The same anulfer serves as the water supply for the Camp Douglas. No contamination has been detected in the wells supplying the base nor private wells adjacent to the base. However, organic carbon levels in the groundwater under, and adjacent to, the pit were measured as high as 700 mg/liter.

Small areas of the pit (ten squares that were one or two feet on a side) were isolated and surfactant solutions applied at a rate of 77 L/m^2 per day for seven days. Cleaning efficiencies were determined based on before and after oil and grease measurements. Full scale air stripping and pilot flushing operations reduced the total organic carbon by as much as 50%. Volatiles in the groundwater were reduced by 99%.

IN SITU FLUSHING & SOILS WASHING TECHNOLOGIES FOR SUPERFUND SITES

Presented at:

RCRA/Superfund Engineering Technology Transfer Symposium

By:

Hazardous Waste Engineering Research Laboratory U.S. Environmental Protection Agency Cincinnati, OH 45268

June 26-27, 1985



CHEMICAL COUNTERMEASURES PROGRAM

"SUPERFUND" RECOGNIZES THE NEED TO DEVELOP COUNTERMEASURES (MECHANICAL DEVICES, AND OTHER PHYSICAL, CHEMICAL, AND BIOLOGICAL AGENTS) TO MITIGATE THE EFFECTS OF HAZARDOUS SUBSTANCES THAT ARE RELEASED INTO THE ENVIRONMENT AND ARE NEEDED TO CLEAN UP INACTIVE HAZARDOUS WASTE DISPOSAL SITES. ONE KEY COUNTERMEASURE IS THE USE OF CHEMICALS AND OTHER ADDITIVES THAT ARE INTENTIONALLY INTRODUCTED INTO THE ENVIRONMENT FOR THE PURPOSE OF CONTROLLING THE HAZARDOUS SUBSTANCE. THE INDISCRIMINATE USE OF SUCH AGENTS, HOWEVER, POSES A DISTINCT POSSIBILITY THAT THE RELEASE SITUATION COULD BE MADE WORSE BY THE APPLICATION OF AN ADDITIONAL CHEMICAL OR OTHER ADDITIVE.

OBJECTIVE

TO DEFINE TECHNICAL CRITERIA FOR THE USE OF CHEMICALS (E.G., SURFACTANTS; NEUTRALIZATION, OXIDATION/REDUCTION, PRECIPITATION AGENTS, ETC.) AND OTHER ADDITIVES (E.G., BIOSTIMULANTS AND BACTERIAL CULTURES) AT RELEASE SITUATIONS SUCH THAT THE COMBINATION OF RELEASED SUBSTANCE PLUS THE CHEMICAL OR OTHER ADDITIVE, INCLUDING ANY RESULTING REACTION OR CHANGE, RESULTS IN THE LEAST OVERALL HARM TO HUMAN HEALTH AND TO THE ENIVRONMENT

Hetre 786

CONVERSION OREGON

PB86-1225

Treatment of Contaminated Soils with Aqueous Surfactants

Science Applications International Corp. McLean, VA

Prepared for

Environmental Protection Agency Cincinnati, OH

Nov 85



Title: Treatment of Contaminated Soils with Aqueous Surfacants Author 1: Ellis, William D. Author 2: Payne, J.R. Author 3: McNabb. G.D. Publisher: Hazardous Waste Engineering Research Laboratory, Office of. Research and Development, USEPA City: Cincinnati, OH Government Report #: EPA/600/2-85/129 Report Order #: PB86-122561 Publication date: 0/1985 Pages: 84 Library of Congress #: TD878 .E47 1985 ID #: 14353620 Location/Employee #: CVO Keywords: 215D0 Solid/Soil/Sediment 216A0 Hydrocarbons 216E0 PCB's 33200 Solids Treatment 33800 In-Situ Treatment

Abstract

14353620

The overall objective of this project was to develop a technical base for decisions on the use of chemical countermeasures at releases of hazardous substances. Work included a literature search to determine the nature and quantities of contaminants at Superfund sites and the applicability of existing technology to in situ treatment of contaminated soils. Laboratory studies were conducted to develop an improved in situ treatment methodology and were designed to determine whether significant enhancement to the efficiency of water washing could be obtained by adding aqueous surfactants to recharge water used in a continuous fecycle.

The use of aqueous nonionic surfactants for cleaning soil spiked with PCBs, petroleum hydrocarbons, and chlorophenol s developed through shaker table and soil column tests. Sontaminant removal from the soil was 92 percent for the CBs, using 0.75 percent each of Adsee 799 copyright (Witco Chemical) and Hyonic NP-90 copyright (Diamond hamrock) in water. For the petroleum hydrocarbons, the "moval with a 2-percent aqueous solution of each surfactant as 93 percent. These removals are orders of magnitude reater than obtained with just water washing and represent significant improvement over existing in situ technology.

reatability studies of the contaminated leachate were also prormed to investigate separating the surfactant from the Intaminated leachate to allow reuse of the surfactant. A