

In Situ Bioremediation of Pesticides in Soil and Groundwater

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Organochlorine pesticides (OCPs) such as DDT, Toxaphene, and Dieldrin are very persistent in the environment and can pose a threat to human health and other living organisms. They adsorb strongly to soils and do not tend to decompose naturally at a significant rate. Through extensive research and many field projects over the past decade, it has been found that the application of solid organic carbon and zero-valent iron (ZVI) to soil and groundwater facilitates the chemical and biological destruction of OCPs. A description of the treatment approach for treatment of soils and groundwater is provided, along with several case studies. © 2008 Wiley Periodicals, Inc.

INTRODUCTION

This article provides a summary of the Adventus Group's experience with treatment of organochlorine pesticides (OCPs) in soil and groundwater using DARAMEND[®] and EHC[®] bioremediation amendments. The firm has offered DARAMEND for treatment of recalcitrant compounds in soil for more than ten years in both *ex situ* and *in situ* applications. Since OCPs bind strongly to the soil matrix, contamination is often limited to the upper few feet of soil, which permits use of readily available equipment for *in situ* application of the DARAMEND amendments. EHC is an injectable version of DARAMEND that has been proven effective for *in situ* treatment of OCPs in groundwater. EHC and DARAMEND support treatment of a number of other inorganic and organic compounds and can therefore be used for mixed impacts. Formulations of these products are also available for simultaneous immobilization of heavy metals such as arsenic, chromium, and lead.

TREATMENT MECHANISMS

Both DARAMEND and EHC contain a patented combination of organic carbon and zero-valent iron (ZVI). Following placement of these amendments into soil or groundwater, the combination generates a reduced environment that supports rapid and complete dechlorination of many chlorinated compounds. Briefly, for treatment of chlorinated solvents, corrosion of ZVI mediates (1) direct chemical dechlorination primarily through *beta*-elimination and hydrogenolysis (Arnold & Roberts, 2000) and (2) generates ferrous iron (Fe⁺²) (Piron, 1991), which is oxidized to ferric iron (Fe⁺³) and subsequently forms reactive precipitates, such as magnetite and green rust (Snoeyink

DARAMEND is an advanced biological treatment technology for soil, sediment, and solid wastes contaminated with recalcitrant organic compounds.

& Jenkins, 1980). In addition, the organic carbon component supports microbial growth, which results in continuous generation of volatile fatty acids (VFAs) that are an excellent carbon source for bacteria involved in enzymatic dehalogenation reactions. Finally, the combination of chemical oxygen consumption (i.e., iron corrosion) and microbial oxygen consumption (i.e., carbon fermentation) enables reliable generation of very low Eh conditions, which enhances both chemical and microbial dehalogenation processes. The most notable difference in treatment effectiveness between the multimechanism, combined ZVI/carbon approach facilitated by EHC and DARAMEND and carbon-alone approaches (e.g., molasses, emulsified vegetable oil, lactate) is that the former generally supports more complete dechlorination without accumulation of metabolites. For example, treatment of trichloroethene (TCE) in groundwater with EHC generally results in complete dechlorination without accumulation of *cis*-1,2-dichloroethylene (*cis*-1,2-DCE) or vinyl chloride. In contrast, most carbon-alone approaches result in varying degrees of accumulation of both metabolites depending on the site conditions. For treatment of OCPs, the pathways are less well defined; however, it is well recognized that dechlorination reactions proceed more rapidly and completely under strong reducing conditions (Dolfing et al., 2008; Seech et al., 1995).

DARAMEND FOR TREATMENT OF OCPs IN SOIL

DARAMEND is an advanced biological treatment technology for soil, sediment, and solid wastes contaminated with recalcitrant organic compounds. The key components of the DARAMEND bioremediation technology are (1) addition of DARAMEND organic amendments to the material to be treated and (2) regulation of oxygen availability and moisture content by mechanical tillage and irrigation, respectively. The treatment schedule and the exact formula of the DARAMEND amendments vary depending on the compound to be treated. For OCPs, an approach with cycled anaerobic and aerobic conditions has been found to be the most effective. For these applications, the DARAMEND soil amendments are composed of organic material (typically 60 to 80 percent by weight), and microscale ZVI (typically 20 to 40 percent by weight). The organic fraction is derived from natural plant fibers rich in cellulose and hemicellulose and, therefore, serves as a carbon source for microbiological consumption. DARAMEND also provides the major, minor, and micro nutrients commonly found in plant material, such as nitrogen, phosphorus, potassium, and trace elements that are required for rapid microbial growth. The amendments are derived from agricultural plant materials and are manufactured regionally to serve international markets (including Australia, Canada, Europe, and the United States) using a proprietary and nonhazardous process.

DARAMEND bioremediation enhances and promotes natural bioremediation rates by adjusting conditions in a soil matrix to stimulate biodegradation of target compounds by indigenous microorganisms. The process is applied in cycles, wherein the contaminant concentrations decrease with each cycle and the number of cycles required to reach the treatment goals depends on the initial concentrations, the responsiveness of the soil to treatment, the amendment application rate, and other factors. Each cycle consists of creating a five-to-ten-day reductive phase followed by a one-to-two-day aerobic phase. The reductive phase involves incorporation of the DARAMEND soil amendment, tillage, and irrigation to approximately 90 percent of the soil's water-holding capacity. Once



Exhibit 1. Placement of soil into treatment cell

irrigation is completed, the soil redox potential drops rapidly and generally reaches Eh levels between -400 and -500 mV. The drop in redox potential is a result of the combined effects of iron oxidation (i.e., Fe^0 to Fe^{+2} and Fe^{+3}) and microbial oxygen consumption. Soil remains in the low Eh phase of a given treatment cycle for between five and ten days to allow time for reductive dechlorination reactions. The treatment cycle is completed with a one-to-two-day aerobic period that is created through introduction of atmospheric oxygen via soil mixing to attain Eh levels of typically $+100$ to $+200$ mV. No microbial inoculation is conducted.

DARAMEND Installation Methods

DARAMEND has frequently been applied to excavated soil and dredged sediment in on-site biotreatment cells (Exhibit 1). The DARAMEND technology can be applied to excavated soil in a number of different formats, including windrows and biopiles, as well as in biotreatment cells.

DARAMEND bioremediation can also be effectively applied *in situ* as a land treatment process. Soil and amendments are blended using a rotary tiller, driven by an agricultural tractor, with an effective penetration of two feet (Exhibit 2). Deeper soil impacts may be treated *in situ* using deep soil mixing equipment or by applying the DARAMEND treatment in lifts. Depending on the cost of excavation and the depth of contamination this may be more cost-effective than *ex situ* treatment. Water content is a critical process parameter and is adjusted using agricultural irrigation equipment (Exhibit 3).

Soil Treatment Performance

As of this writing, DARAMEND has been successfully applied to more than 4 million tons of soil, sediment, and other materials contaminated with persistent organic compounds, including polynuclear aromatic hydrocarbons (PAHs), pentachlorophenol (PCP), phthalates, chlorinated herbicides and pesticides, organic explosive compounds, and wood preservatives at a variety of industrial and military sites in the United States, Canada, and Europe. As the provider of the treatment technology, given its past effectiveness, Adventus is willing to enter into risk-sharing agreements with environmental consultants



Exhibit 2. Application of DARAMEND



Exhibit 3. Irrigation to increase moisture

and site owners in the form of a remedial performance guarantee. The results from a few recently completed pesticide projects are highlighted in Exhibit 4. More detailed case studies of two applications are provided below. The first case study represents an *in situ* application, and the second case study is an example of treatment of excavated soil in an on-site treatment cell.

CASE STUDY #1: *IN SITU* TREATMENT OF DIELDRIN IN SOIL

A remedial effort using cycled DARAMEND treatment for removal of Dieldrin from 2,600 tons of soil was conducted in November 2004 in coastal Florida. The DARAMEND was applied *in situ* using a deep rotary tiller at an application rate of 0.5 percent DARAMEND on a weight-by-weight basis per cycle. Following completion of two treatment cycles, conducted over a period of two to three weeks, the mean Dieldrin concentration in soil, as determined from six sampling locations, was reduced from

Exhibit 4. Influence of DARAMEND bioremediation on various OCPs in soils at sites in Canada and the United States

Site	Compound	Concentration (mg/kg)		Treatment Period
		Initial	Final	
Uniroyal Chemical Ontario, Canada	2,4-D	97	3.8	9 months
	2,4,5-T	8.1	1.3	
	DDT	53.5	4.7	
CIBA-Geigy Ontario, Canada	Metolachlor	72	<1	10 months
	Atrazine	15	<1.5	
W.R. Grace South Carolina, USA	Toxaphene	239	5.1	4 months
	DDT	89	16.5	
THAN Superfund Site Alabama, USA	Toxaphene	189	11	10 months
	DDT	84	9	
	DDD	180	52	
	DDE	25	6	
ATOFINA Chemicals Kentucky, USA	a-HCH	7,647	446	99 days
	b-HCH	1,200	373	
	Lindane	567	14	
	d-HCH	747	57	
	HCB	10.9	1.3	
Former Agricultural Site Florida, USA	Dieldrin	45.9	15.1	<i>In situ</i> /20 days
Future Residential Site Ontario, Canada	DDT	2	0.33	3 weeks
	DDE	3.1	0.7	
	DDD	0.07	0.025	

45.9 $\mu\text{g}/\text{kg}$ to 15.1 $\mu\text{g}/\text{kg}$ (Exhibit 5). Application of a third treatment cycle resulted in additional removal of Dieldrin to a concentration of 5.8 $\mu\text{g}/\text{kg}$, resulting in a total reduction of between 85 and 90 percent. The remedial objective was met at a total product cost of approximately \$12.50/ yd^3 .

CASE STUDY #2: EX SITU TREATMENT OF TOXAPHENE AND DDT IN SOIL

Bioremediation of pesticide-impacted soil/sediment was required at a Superfund site in Alabama. Prior to treatment, Toxaphene, DDT, and DDD exceeded remedial objectives in most areas of the site. Toxaphene and DDD concentrations, in particular, were highly elevated in some areas.

Repeated applications of DARAMEND were employed to generate sequential anoxic and oxic conditions in the soil. Amendments were incorporated to a depth of two feet using a specialized deep rotary tiller. Water was then applied to bring the soil moisture content up to 90 percent of the soil water-holding capacity. These steps were repeated for

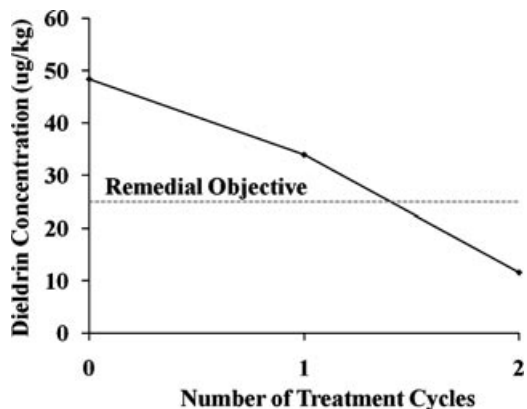


Exhibit 5. *In situ* DARAMEND remediation of Dieldrin-impacted soil

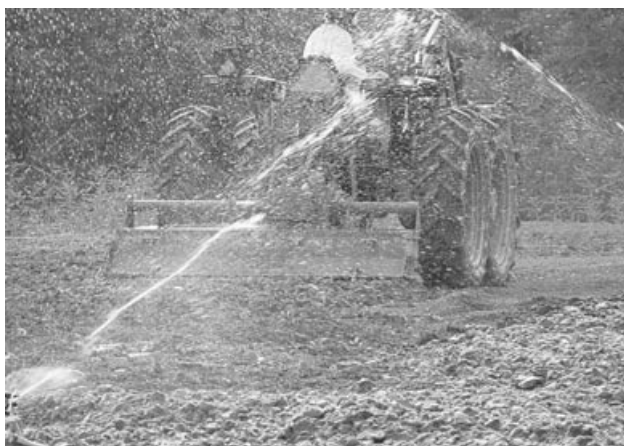


Exhibit 6. Mixing DARAMEND into soil and irrigating to increase moisture

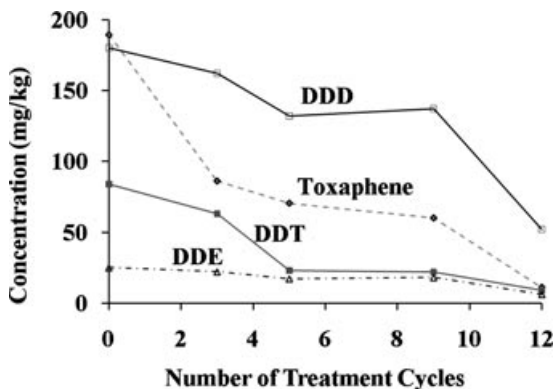


Exhibit 7. Influence of DARAMEND bioremediation on Toxaphene, DDT, DDE, and DDD soil concentrations

each treatment cycle (Exhibit 6). The amendment dosage was 2.2 percent for the first cycle and 0.7 percent for subsequent cycles as needed.

Exhibit 8. Influence of EHC bioremediation on various OCPs in groundwater/saturated soils at sites in the United States

Site	Compound	Concentration		Treatment Period
		Initial/Control	Final/Latest Data	
Pilot-Scale PRB Pesticide Manufacturing Facility, California, USA	Dibromochloropropane [$\mu\text{g/L}$]	1.5	0.26	Ongoing—5 months
	Ethylene dibromide [$\mu\text{g/L}$]	1.5	0.5	
	Nitrate-nitrogen [mg/L]	240	20	
Plume Treatment Using Three Reactive Zones Former Pesticide Manufacturing Facility Southeastern United States	Endrin [$\mu\text{g/L}$]	20.5	0.6	Batch study (detects)—4 days
	pp'-DDD [$\mu\text{g/L}$]	1.3	ND	
Hot-Spot Treatment, Former Pesticide Manufacturing Facility Southeastern United States	pp'-DDT [$\mu\text{g/L}$]	11.9	ND	Field data (mean conc.)—6 months
	Endrin Ketone [$\mu\text{g/L}$]	1.4	ND	
Hot-Spot Treatment, Former Pesticide Manufacturing Facility Southeastern United States	Total BHCs [$\mu\text{g/L}$]	1.1	0.51	Field data (mean conc.)—10 months
	Dieldrin [$\mu\text{g/L}$]	0.6	0.19	
	Endrin [$\mu\text{g/L}$]	0.58	0.36	
Hot-Spot Treatment, Former Pesticide Manufacturing Facility Southeastern United States	Total BHCs + Dieldrin + Endrin [$\mu\text{g/L}$]	2.3	1.1	Mean conc. in saturated soil—8 months
	Toxaphene [mg/kg]	127.7	8.7	
Hot-Spot Treatment, Former Pesticide Manufacturing Facility Southeastern United States	Total OCPs [mg/kg]	169.1	11.8	Mean conc. in saturated soil—8 months

The remedial goals (i.e., Toxaphene—29 mg/kg, DDT—94 mg/kg, DDD—132 mg/kg, and DDE—94 mg/kg) were reached in all areas of the treatment cell following the application of 3 to 12 treatment cycles. The number of treatment cycles required to reach the remedial goal was primarily dependent on the initial concentrations. Analytical results indicate that mean Toxaphene, DDT, DDD, and DDE concentrations were reduced from 189 mg/kg, 81 mg/kg, 180 mg/kg, and 25 mg/kg to 10 mg/kg, 9 mg/kg, 52 mg/kg, and 6 mg/kg, respectively (Exhibit 7). This corresponds to removal and destruction efficiencies (RDEs) of 95, 89, 71, and 76 percent.

In some sampling zones, the initial pesticide concentrations were much higher than the mean concentrations, and performance in these zones was correspondingly more effective. For example, Toxaphene, DDT, DDD, and DDE concentrations were reduced from 720 mg/kg, 227 mg/kg, 590 mg/kg, and 65 mg/kg to 10.5 mg/kg, 15 mg/kg, 87 mg/kg, and 8.6 mg/kg, respectively, in the more heavily impacted regions of the site. This corresponds to RDEs of 99, 94, 85, and 87 percent.

The treatment cost per ton varied according to the initial concentration and ranged between U.S. \$29/ton and \$63/ton. The average unit cost for the treatment of approximately 4,500 tons of soils was approximately \$55/ton.

As indicated above, variable contaminant concentrations resulted in variable treatment time requirements. Remedial goals were reached after three treatment cycles (six weeks) in less heavily impacted regions on the site, while the most heavily impacted

areas required 12 treatment cycles (24 weeks). On average, the remedial goals were achieved following the application of approximately 8 treatment cycles (16 weeks).

EHC FOR CHLORINATED PESTICIDES IN GROUNDWATER

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Derived from the DARAMEND technology, EHC is a combination of controlled-release carbon and zero-valent iron (ZVI) particles used for stimulating reductive dechlorination of otherwise persistent organic compounds in groundwater. Following placement of EHC into the subsurface environment, a number of physical, chemical, and microbiological processes combine to create very strong reducing conditions that stimulate dechlorination of organic solvents and other recalcitrant compounds such as OCPs. First, the organic component of EHC (fibrous organic material) is nutrient-rich, hydrophilic, and has high surface area; thus, it is an ideal support for growth of bacteria in the groundwater environment. As they grow on EHC particle surfaces, indigenous heterotrophic bacteria consume dissolved oxygen, thereby reducing the redox potential in groundwater. In addition, as the bacteria grow on the organic particles, they ferment carbon and release a variety of volatile fatty acids (acetic, propionic, butyric), which diffuse from the site of fermentation into the groundwater plume and serve as electron donors for other bacteria, including dehalogenators and halorespiring species. Finally, the small ZVI particles (<5 to 45 μm) provide a substantial reactive surface area that stimulates direct chemical dechlorination and an additional drop in the redox potential of the groundwater via chemical oxygen scavenging.

These physical, chemical, and biological processes combine to implement *in situ* chemical reduction (ISCR), which stimulates chemical and microbiological dechlorination of otherwise persistent compounds. Redox potentials as low as -550 mV are commonly observed in groundwater after EHC application. At these Eh levels, many organic constituents of interest (COIs) are thermodynamically unstable and will degrade via pathways more typical of physical destruction processes.

EHC is specifically formulated for injection into the subsurface. EHC is provided in 50-lb or 25-kg bags as a dry powder and mixed with water into a slurry. The EHC slurry can be injected into the subsurface using a number of available technologies, including direct injection through GeoProbe[®] rods and hydraulic or pneumatic fracturing. It can also be applied via direct placement into trenches or by using deep soil mixing equipment. Common applications include hot-spot treatment, plume treatment, and plume management using a permeable reactive barrier.

Relevant Groundwater Treatment Performance

EHC has been evaluated at both bench and field scale for treatment of various OCPs in groundwater (Exhibit 8). Please note that the results described here refer to a single application of EHC, and the treatment time refers to the elapsed time post application. A detailed EHC case study is presented in the following section.



Exhibit 9. Application of EHC slurry using direct injection

Exhibit 10. Influence of three months of EHC treatment on TCE and CT concentrations in groundwater (µg/L)

	MW #1	MW #2	MW #3	MW #4	MW #5	MW #6
TCE Pretreatment	<1.0	2.5	1.5	44	<1.0	1
TCE Posttreatment	<1.0	1.1	<1.0	1.3	<1.0	<1.0
CT Pretreatment	<1.0	260	<1.0	3.7	0.34 (est.)	4.2
CT Posttreatment	<1.0	7.8	<1.0	<1.0	<1.0	<1.0

EHC CASE STUDY: TREATMENT OF CHLORINATED SOLVENTS AND PESTICIDES IN GROUNDWATER

Groundwater at a former manufacturing facility was impacted by chlorinated solvents, primarily carbon tetrachloride (CT) and TCE, as well as organochlorinated pesticides. Adventus employed its EHC *in situ* chemical reduction technology to yield safe, rapid, and effective *in situ* treatment.

The aquifer volume requiring treatment was 110 feet wide by approximately 190 feet long, from 15 to 40 feet below ground surface (bgs). The approach was to create three, 10-foot-wide reactive zones that were perpendicular to groundwater flow: one at the upgradient edge and two in the middle of the treatment area. Each reactive zone was created through two rows of direct-push injections (Exhibit 9), spaced five feet apart. The theory behind this reactive zone approach is that the volatile fatty acids, hydrogen, and ferrous iron released from EHC would migrate downgradient to treat the plume. Further, contact between contaminants and the ZVI in EHC would facilitate chemical dechlorination via the *beta*-elimination pathway. A total of 45,000 lbs of EHC were

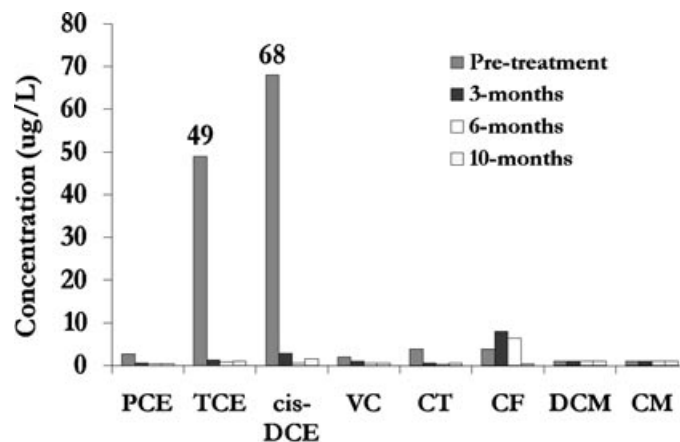


Exhibit 11. Influence of EHC treatment on chloroethene and chloromethane concentrations at MW-2

applied at the site. Within the reactive zones, the application rate was 0.5 percent by dry soil mass; however, the overall application rate for the total area treated was 0.08 percent.

The treatment results are shown in Exhibit 10 where the pretreatment and three-month posttreatment results are presented for all wells in the treatment area. The full range of analyzed chloroethenes and chloromethanes are shown in Exhibit 11 for the most highly contaminated well. All constituents at this well were significantly reduced, with TCE being reduced by 97 percent, from 49 $\mu\text{g}/\text{L}$ to 1.3 $\mu\text{g}/\text{L}$. Exhibit 12 shows the contoured field data for carbon tetrachloride one year prior to injection, and three and six months following the injections. At the six-month sampling event, all VOC treatment goals were met. Exhibit 13 shows the degradation of OCPs over time from all of the monitored wells due to EHC application. Given that OCPs are highly sorbed to soil particles, OCPs in groundwater will be more persistent than VOCs. However, the OCP concentrations are decreasing over time.

The EHC injection was completed in 20 days. Three months following EHC additions, the concentration of chlorinated solvents decreased by as much as 97 percent, and as much as 99.7 percent after six months. The concentrations of all VOCs were below the site cleanup criteria for all sample locations. The EHC product cost was U.S. $\$0.17/\text{ft}^3$ ($\$6.0/\text{m}^3$) of treated aquifer.

SUMMARY

The combination of chemical dehalogenation mechanisms provided by ZVI, with the enzymatic dehalogenation mechanisms enabled when bacteria are provided with a suitable carbon source, results in a robust, multimechanism treatment approach for soil and groundwater contaminated with chlorinated compounds. This combined chemical/biological treatment method has been widely and successfully applied to soil and groundwater environments using the unique iron/carbon products DARAMEND and EHC.

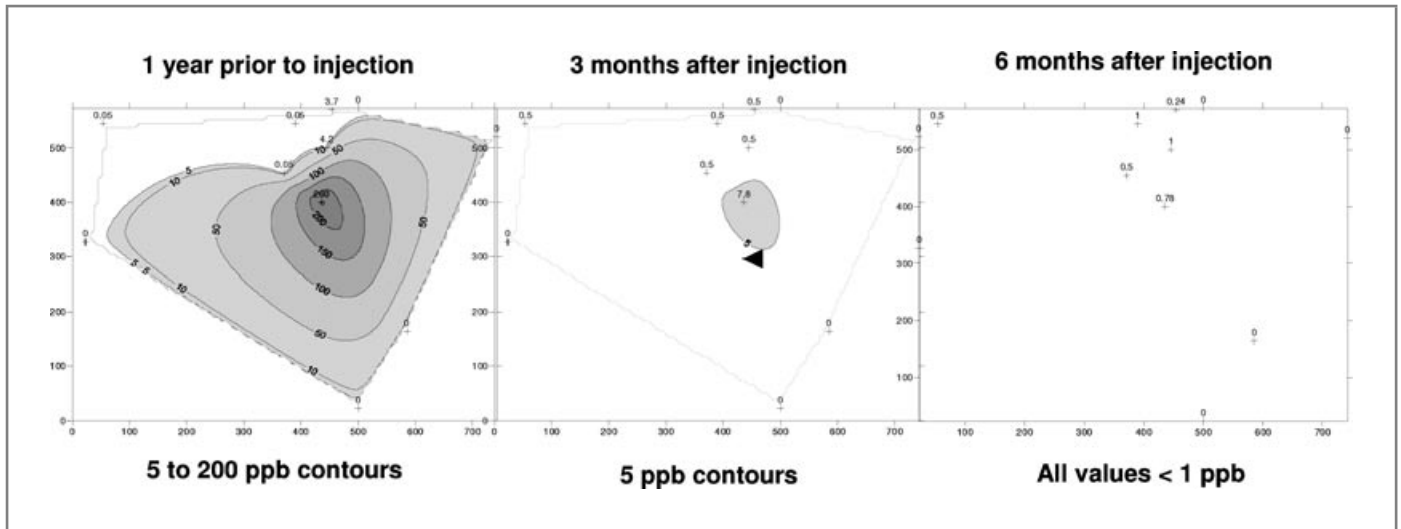


Exhibit 12. Influence of EHC treatment on contoured carbon tetrachloride data

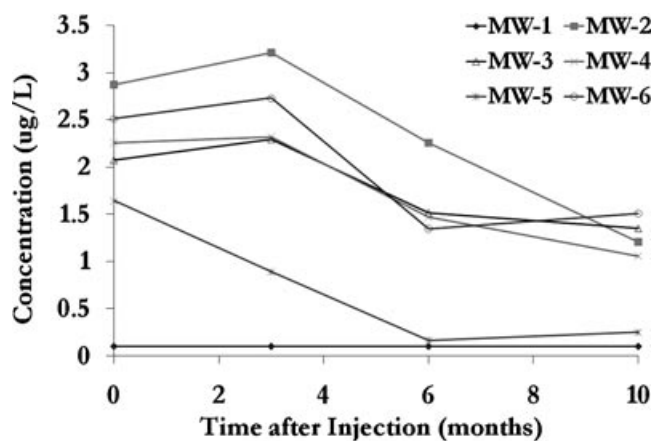


Exhibit 13. Influence of EHC treatment on OCPs in groundwater

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Alan Seech, PhD, is CEO and director of technology at Adventus Group and is an inventor of the patented DARAMEND technology for bioremediation of soils and sediments containing recalcitrant organic contaminants. He holds M.Sc. and PhD degrees in soil chemistry and environmental microbiology, respectively, from the University of Guelph. Dr. Seech has published numerous articles on bioremediation and biodegradation of organic contaminants in soil and presented more than 30 papers at international conferences on bioremediation.

Kerry Bolanos-Shaw, M.Sc., is vice president of operations at Adventus Group. She developed expertise in optimization of multiple bioremediation technologies and has contributed significantly to Adventus's portfolio of proprietary technologies. Bolanos-Shaw's responsibilities include preparation of technical reports and liaison with clients and environmental agencies, research and development, and coordination of manufacturing activities. She received an MS in environmental microbiology from the University of Guelph, Canada, in 1997.

David Hill, M.A.Sc., P.Eng., is the director of operations at Adventus Group. He received a master's degree in civil environmental engineering from the University of Toronto. As a professional engineer, Hill has been intensely involved in the development of the DARAMEND and EHC technologies from an engineering perspective. He has successfully managed many field-scale projects and has presented numerous scientific papers based on those projects at conferences throughout North America.

Josephine Molin, M.Sc., is a project engineer at Adventus Group. Since joining Adventus in 2004, she has been involved with remedial design work and optimizing construction approaches, and has managed a wide range of remediation projects. She received a master's degree in environmental engineering from Uppsala University in Sweden in 2003.
