REMEDIATION OF SOILS IMPACTED BY ORGANOCHLORINE PESTICIDES USING THE DARAMEND TECHNOLOGY

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Abstract

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 a mixture of solid organic carbon and zero-valent iron (DARAMEND®) to soil and groundwater facilitates the chemical and biological destruction of OCPs. The article provides a description of this approach for OCP treatment in soils, along with several case studies.

Key Words: DARAMEND, ZVI, pesticide, in-situ soil treatment

Introduction

This article provides a summary of the Adventus Group's experience with treatment of OCPs in soil and groundwater using DARAMEND® bioremediation amendment. DARAMEND is an advanced biological treatment technology for soil, sediment and solid wastes contaminated with recalcitrant organic compounds. When applied to OCPs, the key to this remedial approach is composition of the DARAMEND soil amendment and application of repeated and sequential anoxic and oxic conditions to the soil matrix. The patented soil amendment is comprised of plant fiber-based organic material and reduced, micro-scale iron (CZ Patent No. 287711). The treatment results in the sequential reductive dechlorination and aerobic biodegradation of chlorinated organic compounds. The amendment is typically applied at low rates (i.e.; <4% w/w) and therefore causes very little, if any, bulking of the soil volume following treatment. Over the last 15 years, the technology has been used successfully for in-situ and ex-situ treatment of soils contaminated with a range of OCPs at sites in North America and Europe.

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 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 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 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.

Installation Methods

DARAMEND has frequently been applied to excavated soil and dredged sediment in on-site biotreatment cells. 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. 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.

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 and site owners in the form of a remedial performance guarantee. The results from a few recently completed pesticide projects are highlighted in Table 1. More detailed case studies of three applications are provided below. The first two case studies represent *in situ* applications, and the third case study is an example of treatment of excavated soil in an on-site treatment cell.

Table 1. Influence of DARAMEND bioremediation on 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-Giegy, 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	
Confidential Client Florida, USA	Dieldrin	0.0459	0.0151	20 days
Confidential Client, Ontario, Canada	DDT	2.05	0.66	3 weeks
	DDE	2.37	0.80	
	Dieldrin	0.110	0.028	

Case Study #1: In Situ Treatment of Dieldrin in Soil

A remedial effort using cycled DARAMEND treatment for removal of Dieldrin from 2,400 tonnes 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 45.9 μg/kg to 15.1 μg/kg (Figure 1). Application of a third treatment cycle resulted in additional removal of Dieldrin to a concentration of 5.8 μg/kg, resulting in a total reduction of between 85 and 90 percent. The remedial objective was met at a total product cost of approximately $16.30/m^3.

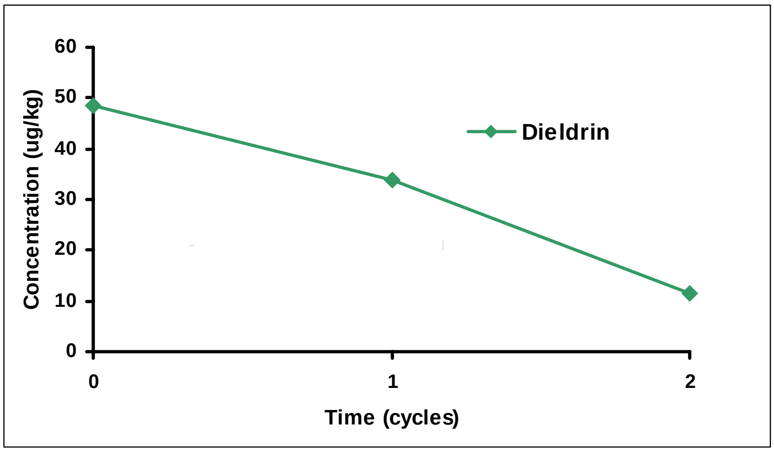

Figure 1. In situ DARAMEND remediation of Dieldrin-impacted soil

Case Study #2: In Situ Treatment of DDT, DDE, and Dieldrin at a Residential Development Site, Ontario, Canada

A residential development was to be built on a former agricultural land, where application of pesticides over many decades of apple trees and strawberry plants resulted in Dieldrin, DDT and DDE residual concentrations in the upper the upper 0.5 m soil that exceeded the standards for residential use.

A successful two-acre (0.8 ha) pilot project was completed in late 2006. By early September 2007, four months after kick-off, the full-scale remediation of an additional 32 acres (13 ha) of soil was completed on time and on budget. The guaranteed fixed-price cost of this turn-key project was less than US$35,000 per acre (less than $23 per tonne). Compared to a theoretical cost of dig and dump of ca. $100/tonne, the savings on the project would be over $87/tonne. The Adventus approach resulted in savings of over $4 million compared to the dig and dump estimate.

The DARAMEND amendment was spread onto the soil and incorporated using specialized rotary tillers. Once incorporated into the soil, water is added to achieve the desired moisture content. At this site, only one or two reductive-aerobic treatment cycles were required per plot to achieve the site remediation targets. The results of the treatment are summarized in Table 1. For plots that were treated in one cycle, the average percentage removal ranged from 38% to 53%. For plots that required two treatment cycles, the average percentage removal was between 65% and 68%. Although DDD did not exceed the remedial standards, it was reduced by an average of 57% in one treatment cycle.

Case Study #3: 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 each treatment cycle. The amendment dosage was 2.2 percent for the first cycle and 0.7 percent for subsequent cycles as needed.

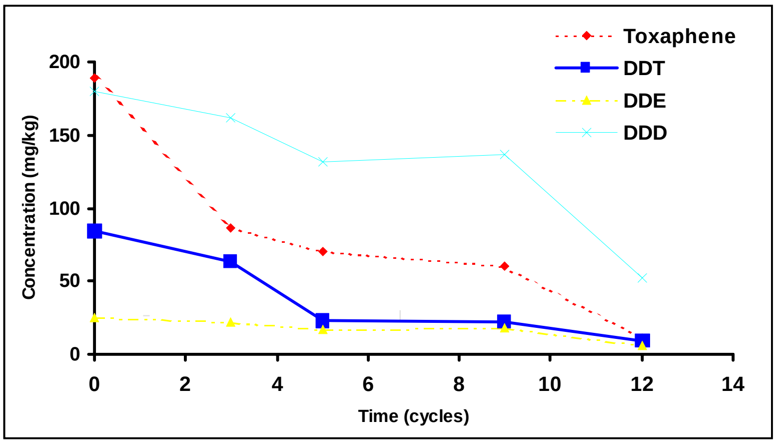

Figure 2. Influence of DARAMEND bioremediation on Toxaphene, DDT, DDE, and DDD soil concentrations

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 (Figure 2). 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 (Figure 2). 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. $32/tonne and $69/ton. The average unit cost for the treatment of approximately 4,100 tonnes of soils was approximately $60/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).

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 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 product DARAMEND. In addition, the treatment method is very environmentally sound. The soil can be treated on site as opposed to using landfill space. The process uses little energy and very few resources. Finally, contaminants are destroyed, not just transported for storage or treatment elsewhere.