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SITE Technology Capsule

GRACE Bioremediation Technologies' DARAMEND™ Bioremediation Technology

Abstract

GRACE Bioremediation Technologies' DARAMEND™ Bioremediation Technology is an amendment-enhanced bioremediation technology for soils and sediments contaminated with a wide variety of organic contaminants including chlorinated phenols, polynuclear aromatic hydrocarbons (PAHs) and petroleum hydrocarbons. The technology may be applied *ex situ* to sediment and soil and *in situ* to near-surface soils. The technology is based upon the addition of solid-phase organic amendments of specific particle-size distribution and nutrient content. The amendments increase the ability of the soil matrix to supply biologically available water and nutrients to microorganisms that are capable of degrading the target compounds. In addition, the amendments bind pollutants to reduce the acute toxicity of the soil's aqueous phase, thereby allowing microorganisms to survive in soils containing very high concentrations of toxicants.

The DARAMEND™ Bioremediation Technology was evaluated under the SITE program at the Domtar Wood Preserving Facility in Trenton, ON, Canada. The facility formerly treated wooden poles with solutions of creosote and pentachlorophenol (PCP). Soil at the site is contaminated with chlorinated phenols and PAHs at concentrations of up to 700 mg/kg and 3,000 mg/kg, respectively.

Results from the SITE Demonstration indicate that the DARAMEND™ Bioremediation Technology significantly reduced total chlorinated phenols (TCPs), PAHs, and total recoverable petroleum hydrocarbons (TRPH) in the contaminated soils. Toxicity tests, using earthworm mortality and seed germination inhibition, indicated that the bioremediation process reduced the toxicity of the soils to these organisms. Water balance was successfully maintained to avoid the generation of contaminant-laden leachate. The DARAMEND™ Bioremediation Technology was implemented without any difficulties and it generally operated well throughout the demonstration period.

The DARAMEND™ Bioremediation Technology was evaluated based on seven criteria used for decision making in the Superfund feasibility study (FS) process. Results of the evaluation are summarized in Table 1.

Introduction

In 1980, the U.S. Congress passed the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), also known as Superfund, which was committed to protecting human health and the environment from uncontrolled hazardous waste sites. CERCLA was amended by the Superfund Amendments and Reauthorization Act (SARA) in 1986, which calls for long-term effectiveness and permanence of remedies at Superfund sites. SARA mandates implementing permanent solutions and using alternative treatment technologies or resource recovery technologies, to the maximum extent possible, to clean up hazardous waste sites.

State and federal agencies, as well as private parties, are now exploring a growing number of innovative technologies for treating hazardous wastes. The sites on the National Priorities List total over 1,700 and represent a broad spectrum of physical, chemical, and environmental conditions requiring various types of remediation. The U.S. Environmental Protection Agency (EPA) has focused on policy, technical, and informational issues in exploring and applying new remediation technologies to Superfund sites.

One such initiative is EPA's Superfund Innovative Technology Evaluation (SITE) program, which was established to accelerate development, demonstration, and use of innovative technologies for site clean-ups. EPA SITE Technology Capsules summarize the latest information available on selected innovative treatment and site remediation technologies and related issues. These Capsules are designed to help EPA Remedial Project Managers, EPA On-Scene Coordinators, contractors, and other site clean-up managers understand the

Table 1. FS Criteria Evaluation for the DARAMEND™ Bioremediation Technology

Overall Protection of Human Health and the Environment	*Compliance with Federal ARARs*	*Long-Term Effectiveness and Permanence*	*Reduction of Toxicity, Mobility, or Volume Through Treatment*	*Short-Term Effectiveness*	*Implementability*	*Cost*
Provides both short- and long-term protection by eliminating organic (PAHs and TCPs) contaminants in soil.	*Requires compliance with RCRA treatment, storage, and land disposal regulations (of a hazardous waste).*	*Provides for irreversible treatment of PAHs and TCPs.*	*Significantly reduces toxicity, mobility, and volume of soil contaminants through treatment.*	*Bioremediation processes require time for the degradation of contaminants. Length of time is based on contaminant type, concentration levels, and the characteristics of the media.*	*Involves few administrative difficulties.*	*A first estimate of costs is $50 to $80 USD/ton. The cost is affected by project parameters such as contaminant type and initial concentration; contaminant target concentration; soil volume requiring remediation; climate; remediation time frame; and project scope of work.*
Removes existing contamination source, thereby preventing continual contamination to other environmental media.	*Excavation, construction, and operation of onsite treatment unit may require compliance with location specific ARARs.*	*Prevents further ground-water contamination and pollutant migration.*	*Eliminates contamination source, thus reducing the mobility of contaminants to other environmental media.*		*System is easy to install and operate. Uses conventional excavation and tilling equipment.*	
Requires measures to protect workers and community during excavation, handling, and treatment.	*Process does not generate significant air emissions or wastewater during implementation or treatment.*		*Volume of soil after treatment is slightly increased due to the addition of treatment amendments.*		*May require a green house type enclosure to enhance moisture control and raise the soil temperature (in cold climates)*	

types of data and site characteristics needed to effectively evaluate a technology's suitability for cleaning up Superfund sites.

This Capsule provides information on the DARAMEND™ Bioremediation Technology. The technology may be applied to the remediation of soils and sediments contaminated with a wide variety of organic contaminants including chlorinated phenols, PAHs, and petroleum hydrocarbons. The technology may be applied *ex situ* to sediment and soil and *in situ* to near-surface soils. The bioremediation process has three components: addition of a solid phase organic soil amendment, homogenization and aeration of the soil/amendment using specialized tilling equipment, and maintenance of soil moisture. GRACE Bioremediation Technologies' DARAMEND™ Bioremediation Technology was evaluated under EPA's SITE program during an 11-mo period from October 1993 to September 1994 at the Domtar Wood Preserving Facility in Trenton, ON, Canada. The DARAMEND™ technology was evaluated to assess its effectiveness in treating excavated soils contaminated with chlorinated phenols (mainly pentachlorophenol) and PAHs. Information in this Capsule is based on specific site characteristics and results of the SITE Demonstration at the Domtar site. This Capsule presents the following information:

- Abstract
- Technology description
- Technology applicability
- Technology limitations
- Process residuals
- Site requirements
- Performance data
- Technology status
- Sources of further information

Technology Description

The DARAMEND™ Bioremediation Technology treats soils and sediment contaminated with a wide variety of organic contaminants including chlorinated phenols, PAHs, and petroleum hydrocarbons. The process accelerates degradation of the target compounds by stimulating indigenous soil microbes. In addition, the process allows remediation to proceed in toxic soils contaminated with high levels of PCP.

Technology application requires contaminated soil to be screened to approximately 10 cm to remove debris (rocks, wood, metal) that could interfere with the incorporation of the organic amendments. *In situ*, the soil is screened to a depth of 60 cm using equipment such as subsurface combs and agricultural rock pickers. *Ex situ*, the soil is passed over a mechanical screen. For *ex situ* applications, screened soil is transported to the treatment area and deposited into a low permeability cell (a high density polyethylene-lined earthen cell or a concrete cell). The contaminated soils, to a maximum depth of 0.6 m, are mixed with amendments and periodically tilled and irrigated to encourage the growth of contaminant-degrading microbiota. A cover may be used to control soil moisture content and eliminate run-on/run-off. Covering the plot has the added benefit of raising soil temperature to accelerate remediation in cold climates. Irrigation and tillage continue until the concentrations of target compounds have fallen below mandated cleanup levels. The length of time required for remediation is based on many factors including the type and concentrations of contaminants, soil temperature, and soil chemistry.

The DARAMEND™ Bioremediation Technology consists of three innovative processing components which, in tandem, constitute the remediation technology:

- Addition of solid-phase organic soil amendments of specific particle-size distribution and nutrient content.
- Distribution of the soil amendments through the target matrix and the homogenization and aeration of the target matrix using specialized tilling equipment.
- A specialized soil moisture control system designed to maintain moisture content within a specified range to facilitate rapid growth of an active microbial population and prevent the generation of leachate.

The organic amendments increase the ability of the soil matrix to supply biologically available water and nutrients to microorganisms that are capable of degrading the target compounds. The amendments also bind pollutants to reduce the acute toxicity of the soil's aqueous phase, thereby allowing microorganisms to survive in soils containing very high concentrations of toxicants.

Selection of a soil amendment is based on treatability and pilot-scale investigations, because the physical and chemical properties of the target soil dictate the type of amendment to be used. Relevant soil physical properties include textural variation, percent organic matter, and moisture content. Relevant soil chemical properties include soil pH, macro- and micronutrients, metals, and the nature and concentration of soil contaminants.

Periodic tilling of the soil increases diffusion of oxygen to microsites and ensures uniform distribution of irrigation water in the soil. Tilling is performed immediately after amendment addition and at 2-wk intervals thereafter.

Soil moisture is maintained within a specific range below the soil's water holding capacity. Maintenance of soil moisture within this narrow range is critical to effective biodegradation of the target compounds. In the presence of excess moisture, diffusion of oxygen through the soil matrix to microbially active microsites can be limited by a low ratio of air-filled to water-filled pores. Conversely, if soil moisture falls below the optimum range biodegradation can be inhibited because of inadequate biologically available water.

Technology Applicability

The DARAMEND™ Bioremediation Technology is applicable to a wide range of organic contaminants deposited to soil or sediment. The technology has been applied to soils at pilot-scale with total PAH concentrations up to 18,500 mg/kg, total petroleum hydrocarbons up to 8,700 mg/kg, and pentachlorophenol to 660 mg/kg. PAHs, total petroleum hydrocarbons and pentachlorophenol have been reduced to meet Canadian guidelines for industrial soils. Under the Great Lakes Clean up Fund's Contaminated Sediment Treatment Technology Program, GRACE Bioremediation Technologies' DARAMEND™ Bioremediation Technology treated 150 tons of dredged harbor sediment. In approximately 300 days of *ex situ* treatment the level of total PAH contamination was reduced from approximately 1,000 mg/kg to 100 mg/kg – a removal efficiency of approximately 90%. Bench-scale work has resulted in the development of new technology for remediation of soil and sediment contaminated with phthalates, organochlorine pesticides and organic explosives. For example, total phthalates were reduced from 7,710 mg/kg to 47 mg/kg in soil, p,p-DDT, an organochlorine pesticide, was reduced from 684 mg/kg to 1.9 mg/kg in soil and 2,4,6-trinitrotoluene (TNT), an organic explosive, was reduced from 7,200 mg/kg to 19 mg/kg in soil, all exhibiting a greater than 99% removal efficiency.

Technology Limitations

The DARAMEND™ Bioremediation Technology appears to be limited to soils contaminated with non-halogenated and certain halogenated organic compounds. The technology may become technically or economically infeasible when dealing with soils with excessively high contaminant concentrations. The developer claims that the technology would probably not treat soils contaminated with polychlorinated biphenyls (PCBs) or highly halogenated organics. In addition, high levels of heavy metals, soil pH <2, and excessive amounts of buried debris may limit the rate at which biodegradation proceeds. Furthermore, the *in situ* application of the technology is limited to the depth to which the soil can be physically tilled. *Ex situ* applications of the technology may be limited by community acceptance of the inherent hazards (e.g., noise, dust, etc.) associated with excavation activities.

Of course, a number of natural physical and chemical factors may affect the activity and longevity of contaminant-degrading microorganisms in general. The DARAMEND™ Bioremediation Technology addresses many of these factors directly (i.e., moisture content, soil particle size distribution, clay content, nutrient limitations, and oxygen limitations). In addition, some factors (i.e., temperature) are indirectly addressed by implementation of the DARAMEND™ Bioremediation Technology. For instance, a cover (i.e., greenhouse) used for moisture control also adds inherent heat value.

Process Residuals

Large particles of debris, stone, and construction material that are removed from the site prior to bioremediation may require disposal. Otherwise, virtually no solid waste streams are generated by the DARAMEND™ Bioremediation Technology.

If a treatment area cover (i.e., greenhouse) is not used, excessive precipitation in the treatment area may generate leachate or storm water run-off. Excess precipitation is contained in the lined treatment cell and is minimized by the soil moisture control system.

Volatile organic compound emissions may increase during soil tilling. However, previous studies by the developer have indicated that these emission levels are below permissible exposure limits.

Site Requirements

The key requirements for the application of the technology are available utilities and space.

The utilities required are a source of water (either city, surface, or subsurface) and electricity rated at 115 V. Water is used primarily for irrigation but also for dust control and decontamination. When a greenhouse is used as a cover for the treatment plot, electricity is required for fans that separate the two layers of polyethylene in the greenhouse cover.

Cleared land is required for the treatment area, pretreatment (i.e., screening) equipment, temporary storage of debris removed from the soil, and storage of the tillage equipment.

Simple laboratory equipment (i.e., ovens and pH meters) on-site is advantageous but not necessary.

Common to all remediation technologies are office, toilet, and decontamination facilities.

Performance Data

The GRACE Bioremediation Technologies' DARAMEND™ Bioremediation Technology SITE Demonstration was conducted to evaluate the performance of the developer's technology in remediating excavated soils contaminated with PAHs and chlorinated phenols from the Domtar Wood Preserving Facility in Trenton, ON, Canada. The Domtar Wood Preserving Facility formerly treated wooden poles with solutions of creosote and pentachlorophenol. No wood has been treated at the Domtar site since 1990. The facility is presently used to stockpile wooden poles and railroad ties.

According to the developer, the DARAMEND™ technology is an effective bioremediation alternative for the treatment of soils containing levels of chlorinated phenols and PAHs typically considered too toxic for bioremediation.

The developer claimed that the DARAMEND™ Bioremediation Technology could achieve a 95% reduction in total PAHs and a 95% reduction in total chlorophenols over an 8-mo period. Performance was evaluated by comparing the pre- and post-treatment concentrations of each list of analytes presented below:

Total PAHs	Total Chlorophenols (TCPs)
naphthalene	2-chlorophenol
acenaphthylene	2,4-dichlorophenol
acenaphthene	2,4,6-trichlorophenol
fluorene	2,4,5 trichlorophenol
phenanthrene	pentachlorophenol
anthracene	
fluoranthene	
pyrene	
benzo(a)anthracene	
chrysene	
benzo(b)fluoranthene	
benzo(k)fluoranthene	
benzo(a)pyrene	
indeno(1,2,3-c,d)pyrene	
debenzo(a,h)anthracene	
benzo(g,h,i)perylene.	

Since the process is temperature-dependent, the treatment period of 254 calendar days included only the days when the average daily soil temperature within the greenhouse was above 15° C.

The SITE Demonstration was designed to determine whether the developer's claim could be achieved during a full-scale field application of the technology. To evaluate the developer's claims two test plots were constructed and used for this demonstration: a 6 x 36 m Treatment Plot and a 2 x 6 m No-Treatment Plot. Both the Treatment and No-Treatment Plots were underlain with a high-density polyethylene liner (impermeable to the target compounds). This liner was underlain with 10 cm of screened sand to prevent structural damage to the liner. Another 15-cm thick sand layer and a 4-mm thick fiber pad were spread on top of the liner to minimize the potential for direct contact between the liner material and tillage equipment. The target test soil was then screened to less than 1-in. diameter and deposited on top of the sand layer to a thickness of 0.5 m across both plots. The No-Treatment Plot was isolated from the Treatment Plot by wooden partitions and covered with plastic sheeting. The Treatment Plot underwent treatment with the DARAMEND™ technology while the No-Treatment Plot received no treatment and was left idle throughout the demonstration period.

The demonstration objective was accomplished by comparing the total concentrations of select PAHs and of chlorinated phenols prior to application of the DARAMEND™ technology and after approximately 11 mo (254 days) of treatment. Four sampling events were implemented during the course of this study: a baseline event in October 1993, an initial intermediate event in April 1994, a second intermediate event in June 1994, and the final event in September 1994.

The Treatment Plot was subdivided into 54 2x2 m subplots. Soil samples for critical analyses were collected from 18 subplots within the Treatment Plot throughout the demonstration. These subplots were selected using a random number generator. Homogenized soil cores from each of the 18 subplots were analyzed for Semivolatile Organic Compounds using SW846 Method 3540/8270.

Other objectives of the demonstration included determining the toxicity of the soil to earthworms and seed germination in each of the SITE Demonstration plots before and after treatment, monitoring the fate of TRPH in each of the SITE Demonstration plots, monitoring general soil conditions (i.e., nutrients, toxics) that might inhibit or promote process effectiveness, monitoring for leachate within the SITE Demonstration Treatment Plot, monitoring each of the SITE Demonstration plots for active microbial populations, and monitoring the upper sand layer in contact with the treated soil to qualitatively assess any tendency for downward migration of contaminants.

Results from the SITE Demonstration indicate that the DARAMEND™ Bioremediation Technology significantly reduced PAH, TCP, and Total Recoverable Petroleum Hydrocarbons (TRPH) in the Treatment Plot. PAHs were reduced from 1,710 mg/kg to 98 mg/kg (94.3% reduction), total chlorophenols were reduced from 352 mg/kg to 43 mg/kg (87.8% reduction), and total recoverable petroleum hydrocarbons were reduced from 7,300 mg/kg to 932 mg/kg (87.3% reduction).

Results from the No-Treatment Plot indicate no significant decreases in TCPs and TRPH in the soil. Total chlorophenols remained at approximately 217 mg/kg, and TRPH remained at approximately 5,000 mg/kg. However, polyaromatic hydrocarbons were reduced from 1,312 mg/kg to 776 mg/kg, representing a 40.9% reduction. Table 2 summarizes the analytical results from the demonstration.

Toxicity tests were performed on baseline and post-remediation soil samples to determine if the toxicity of the soil had decreased due to the DARAMEND™ Bioremediation Technology. Two toxicity tests were used: germination inhibition of lettuce and radish seeds, and earthworm mortality. The DARAMEND™ Bioremediation Technology appeared to reduce the toxicity of the contaminated soil to both the plant seeds and the earthworms. Toxicity tests indicate that the baseline soils in the Treatment and No-Treatment Plots were toxic to the test organisms. Post-remediation soil toxicity was only slightly reduced in the No-Treatment Plot, while soil in the Treatment Plot was essentially non-toxic to the earthworms and radishes and only slightly toxic to lettuce germination at the end of the study. The slight reduction in toxicity of the No-Treatment Plot is consistent with the slight reductions in PAHs observed. Tables 3 and 4 present the results of the toxicity tests.

The DARAMEND™ Bioremediation Technology did not generate leachate. Water balance was successfully maintained to avoid the generation of contaminated leachate. If generated, this leachate would require treatment prior to discharge.

The DARAMEND™ Bioremediation Technology was implemented without any difficulties and it generally operated well throughout the demonstration period. One exception was the mixing of some of the underlying sand into the soil/amendment mixture during tilling. This resulted in an overall increase in the volume of soil/amendment at the end of the study.

Technology Status

The DARAMEND™ technology has successfully remediated 1,500 tons of soil *ex situ* and 3,500 tons of soil *in situ* (2 ft of near-surface soil) at the former Domtar Wood Preserving Facility. The remediated soil met clean-up criteria set by the Canadian Council of Ministers for the Environment, including a 5 mg/kg criterion for PCP. In 1995, treatment of a second 1,500-ton batch of soil was initiated at the site. Also in 1995, full-scale treatment of 2,500 tons of soil was initiated at a former wood preserving site in eastern Canada.

In the United States during 1996, the DARAMEND™ technology was successfully applied at full scale at a former wood preserving site in Minnesota. Late in 1996, a large-scale field treatability demonstration was initiated in association with remedial actions at the Montana Pole Superfund site in Butte, MT. Commencement of a full-scale project is planned for the summer of 1997 in Washington state.

Key developmental work on the technology is focusing on improving kinetics and expanding applicability with respect to contaminant type. The range of contaminants effectively dealt with by the DARAMEND™ technology has now been expanded to include phthalates. Concentrations of phthalates have been rapidly reduced from thousands to less than 100 mg/kg during bench-scale studies and pilot-scale work at a site in New Jersey in 1996.

In addition, a second generation DARAMEND™ technology has been developed by GRACE Bioremediation Technologies. The new technology rapidly reduces concentrations of organochlorine pesticides (e.g., DDT and Toxaphene™) and organic explosives (e.g., TNT) in soil. Extensive laboratory testing has been completed. Pilot-scale pesticide projects commenced in 1996 in South Carolina and Ontario, Canada, and will continue in 1997. A pilot-scale project to demonstrate remediation of explosives-contaminated soil is expected to commence in 1997.

Table 2. *Results from the DARAMEND™ SITE Demonstration*

Baseline Analyte	Sampling 1 October 1993	Sampling 2 April 1994	Post Treatment June 1994	September 1994	Overall % Reduction
			Treatment Plot		
Total PAHs	1,710	619	221	98	94.3
TCPs	352	158	90	43(13.6)[1]	87.8(96.1)[1]
TRPH	7,300	NA	NA	932	87.3
No Treatment Plot					
Total PAHs	1,312	1,155	982	776	40.9
TCPs	217	288	356	218 (240)[1]	0(0)[1]
TRPH	5,000	NA	NA	5,200	0

All data is mg/kg on a dry weight basis.
NA - Not analyzed.
PAHs - Polynuclear Aromatic Hydrocarbons.
TCPs - Total Chlorinated Phenols.
TRPH - Total Recoverable Petroleum Hydrocarbons.
[1] - Data provided by GRACE Bioremediation Technologies, based on analyses of split samples by an independent laboratory.

Table 3. *Mortality of the Earthworm, Eisenia Foetida, from 28-Day Soil Toxicity Tests*

	Mean Percent Mortality	
	DARAMEND™ Treated Soil	Untreated Soil
Baseline (October 1993)	100% (0%)	100% (0%)
Post-Treatment (September 1994)	0% (3%)	100% (3%)

Values reported are the mean percent mortality in the 100% treated and untreated soil before and after remediation. Paired negative control mortality is in parentheses.

Table 4. *Inhibition of Germination from 5-Day Soil Toxicity Tests Conducted with Lettuce (Lactuca Sativa) and Radish (Raphanus Sativus)*

	Mean Percent Inhibition of Germination			
	DARAMEND™ Treated Soil		Untreated Soil	
	Lettuce	Radish	Lettuce	Radish
Baseline (October 1993)	100% (8%)	52% (4%)	97% (5%)	82% (9%)
Post-Treatment (September 1994)	33% (5%)	0% (1%)	92% (5%)	23% (1%)

Values reported are the mean inhibition of germination in 100% untreated and treated soil before and after remediation. Paired negative control inhibition of germination is in parentheses.

Source of Further Information

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