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The Bioremediation and Phytoremediation of Pesticide-contaminated Sites

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NOTICE

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FOREWORD

Bioremediation and phytoremediation are innovative technologies that have the potential to alleviate numerous pesticide contamination problems. EPA's Technology Innovation Office (TIO) provided a grant through the National Network for Environmental Management Studies (NNEMS) to prepare a technology assessment report on the use of bioremediation and phytoremediation for the cleanup of pesticide-contaminated sites. This report was prepared by a first year graduate student from the University of Montana during the summer of 2000. It has been reproduced to help provide federal agencies, states, consulting engineering firms, private industries, and technology developers with information on the current status of this technology.

About the National Network for Environmental Management Studies (NNEMS)

NNEMS is a comprehensive fellowship program managed by the Environmental Education Division of EPA. The purpose of the NNEMS Program is to provide students with practical research opportunities and experiences.

Each participating headquarters or regional office develops and sponsors projects for student research. The projects are narrow in scope to allow the student to complete the research by working full-time during the summer or part-time during the school year. Research fellowships are available in Environmental Policy, Regulations and Law; Environmental Management and Administration; Environmental Science; Public Relations and Communications; and Computer Programming and Development.

NNEMS fellows receive a stipend determined by the student's level of education and the duration of the research project. Fellowships are offered to undergraduate and graduate students. Students must meet certain eligibility criteria.

About this Report

This report is intended to provide a basic summary and current status of bioremediation and phytoremediation technologies for the treatment of pesticide-contaminated media. It contains information gathered from a range of currently available sources, including project documents, reports, periodicals, Internet searches, and personal communication with involved parties. No attempts were made to independently confirm the resources used.

While the original report included color images, this copy is printed in one color. Readers are directed to the electronic version of this report to view the color images; it is located at **http://clu-in.org**.

ACKNOWLEDGMENTS

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PURPOSE

The intent of this report is to discuss the current state of remediation technologies available for the cleanup of pesticide-contaminated sites. Discussion will focus on, but will not be limited to, the persistent organic pollutants (POPs) identified by the United Nations Environmental Program and remediation technologies that involve bioremediation and phytoremediation. The case studies discussed in this report will consider the advantages and disadvantages of these technologies based upon their application and performance in the field.

PERSISTENT ORGANIC POLLUTANTS

Increasing environmental awareness has resulted in regulatory measures that aim to remedy past mistakes and protect the environment from future contamination and exploitation. These measures intend to preserve the environment and protect human health. Many of the pollutants of concern are toxic, and subsequently, were banned when it was discovered that they were hazardous to human health. Unfortunately, in many cases, these compounds are also persistent in nature. Long after their use has been discontinued, these chemicals remain in soils and sediments where they can enter the food chain directly or percolate down to the water table. Once in the groundwater, these pollutants can enter drinking water wells and cause health problems. These chemicals are also subject to long-range atmospheric transport. One of the primary concerns is the ability of these chemicals to bioaccumulate within the adipose tissue of animals. Indirect accumulation or biomagnification in higher trophic level organisms, such as mammals, may cause health problems over time because of the increasing levels of toxic compounds within the body.

A degree of persistence is often desired in chemicals such as pesticides. If microorganisms degraded them as soon as they were applied, then they would not serve their desired function. There are two main reasons that these compounds persist in nature. First, the conditions necessary for their biodegradation are not present. The microorganisms that are capable of biodegrading these toxic compounds may be absent at the contaminated site. If the necessary microorganisms are present, some limiting factor, such as a nutrient shortage, may create unfavorable conditions for the biodegradation of the contaminant. Various cleanup methods, which will be discussed later, have been devised in order to overcome these limitations in order to make bioremediation more effective. The second possibility is that the compound could be recalcitrant, or resistant to biodegradation. Compounds are recalcitrant for a number of reasons. The compound may be unable to cross the cell membrane for breakdown by intracellular microbial enzymes. Most persistent pollutants are synthetic, and consequently, the structure of these molecules can be vastly different from naturally occurring structures. If microorganisms have only been exposed to these new and unique molecular formations for the last few decades, then they probably have not had enough time to evolve the mechanisms to detoxify or metabolize them.

Whatever the mechanism of persistence, these highly stable organic pollutants are widely recognized as a problem. The United Nations Environmental Program (UNEP) convened four sessions of the Intergovernmental Negotiating Committee (INC) to address this issue (1). One hundred twenty-one countries and 81 non-governmental organizations participated in the most

recent meeting, and the final meeting of the INC is scheduled for December of 2000. The goal of these meetings is to negotiate the UNEP Global Treaty on Persistent Organic Pollutants (POPs), which ultimately aims to eliminate the production and use of all of these toxic chemicals. The INC has established two groups to aid in the negotiation of the treaty. The first group is the Critical Experts Group that will be responsible for determining criteria for the pollutants and identifying which pollutants will be included in the treaty in the future. Twelve pollutants have been selected for the list thus far: aldrin, chlordane, dichlorodiphenyl trichloroethane (DDT), dieldrin, dioxins, endrin, furans, heptachlor, hexachlorobenzenes, mirex, polychlorinated biphenyls (PCBs), and toxaphene. DDT is the exception to the restrictions of the proposed treaty because of its importance in controlling malaria carrying mosquitos in tropical nations. It will slowly be phased out while a replacement is found. These pollutants are pesticides, industrial chemicals and unintended byproducts of combustion and industrial processes. The second group is the Implementation Group, which will approach the technical and financial issues associated with implementing this treaty throughout developing and transitional countries.

Independently, and prior to the UNEP negotiations, the United Nations Economic Commission for Europe (UN-ECE) completed negotiations in February 1998 for a legally-binding regional POPs agreement. Under this agreement, the member countries will reduce, control or eliminate discharges and emissions of persistent organic pollutants (2). They have identified chemicals that are toxic, persistent, bioaccumulate and have the potential for long-range transboundary atmospheric transport as the POPs of concern (2). Persistence is defined as a half-life in soil that is greater than six months and in water that is greater than two months by the UN-ECE (2). Both the UN-ECE and the UNEP negotiations show an increased awareness of the danger of these compounds and the importance in reducing and eliminating them globally.

PESTICIDES

The term pesticide encompasses a variety of different types of chemicals including herbicides, insecticides, fungicides, and rodenticides, among others. Although wood preservatives are regulated as pesticides, they will not be considered here. In 1940, 140 tons of pesticides were used (3). At that time, the most commonly used pesticides were organics such as plant extracts, and inorganics, which contain heavy metals. During the mid-1940s the production and use of synthetic organic pesticides rapidly increased. By 1991, there were approximately 23,400 pesticide products registered with the U.S. Environmental Protection Agency (EPA) (3). In 1997, 1.2 billion pounds of pesticides were used. The agriculture industry used 77%, industrial, commercial and government organizations used 12% and private households used the remaining 11%. (4).

REGULATION OF PESTICIDES

The Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), regulates pesticide production and use in the U.S. All pesticides are registered with the EPA and are assessed to insure that they do not present an unreasonable risk to human health or the environment. When a pesticide is registered, it is also classified as either general or restricted use. The EPA requires older pesticides to be re-registered to confirm that they meet the current data requirements. Most of

the POPs identified by the International POPs treaties are not subject to re-registration because their use is banned.

Part of the registration and re-registration process requires the manufacturer to determine the environmental fate or persistence of the compound. The half-life of the compound is determined for aerobic and anaerobic soil metabolism and for photolysis. Some compounds are also analyzed to determine their field half-life. The varying half-lives are then considered together to give a range for the half-life of the compound. The re-registration fact sheet for metolachlor estimates a half-life between 7 and 292 days in surface soil (5). However, a shallow (60cm) metolachlor-contaminated control plot used during the Superfund Innovative Technology Evaluation of the Daramend™ technology in Ontario, Canada, showed no change in metolachlor concentrations after 565 days (6). In the case of the Daramend™ demonstration, the pesticide was not freshly added as in the fate studies by the pesticide manufacturer. The pesticides in the demonstration have been present in the soil for an extended period of time and have become tightly bound to the soil and thus less bioavailable. This explains the difference in half-life but demonstrates that these environmental fate studies do not always duplicate the conditions that are experienced in the field and are only broad estimates. According to the re-registration fact sheet for heptachlor, it is not subject to environmental fate analysis because of its restricted uses (7). Currently, the only use for which heptachlor is permitted in the U.S. is for the control of fire ants in underground cable boxes and pad-mounted electric power transformers. Most general uses for this chemical were canceled in 1978. Since then it has been placed on the UNEP's list of persistent organic pollutants. Despite the lack of information on the environmental fate of heptachlor and the decrease in its use, this pesticide still persists in the environment. It has been the subject of remediation efforts at several Superfund sites and is the subject of several bioremediation and phytoremediation lab studies (8,9,10,11). In Hawaii, soil samples from agricultural lands show unhealthy levels of Heptachlor and heptachlor epoxide 15 years after it use was discontinued (8). As a result of these persistent residues, crops grown on these sites were destroyed in 1999 after heptachlor epoxide was detected in unhealthy levels on vegetables intended for human consumption (8).

HEALTH CONCERNS

Persistent pesticides pose a threat to the well-being of the environment and to human health. The solid organochloride insecticides are known to accumulate in human adipose tissue. Some of these insecticides, including chlordane, can even be absorbed dermally (12). Other health problems caused by exposure to the solid organochloride insecticides are convulsions, a hyperexcitable state of the brain and a predisposition to cardiac arrhythmia. Eating wheat treated with hexachlorobenzene, another organochloride insecticide, has been associated with human dermal toxicity, which can result in blistering of the skin. Although not all solid organochloride insecticides are considered POPs, many of them are among the compounds on the UNEP's list of persistent organic pollutants, including aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzenes, mirex and toxaphene.

The solid organochloride insecticides are not the only group of pesticides of concern. The triazine pesticides are classified by the EPA as possible human carcinogens (13). They are somewhat persistent in water and mobile in soil (13). In the Midwest, exposure to drinking water

contaminated by triazines is of concern because residuals of these pesticides are among the most frequently detected pesticides in groundwater (13). The EPA and pesticide manufacturers in the U.S. are responding to possible human health risks by phasing out one triazine pesticide, cyanazine, and increasing the restrictions on another, known as atrazine (13).

Many other pesticides of concern are found at contaminated sites. Organophosphates are insecticides that can affect nervous system function (14). Nitrophenolic and nitrocresolic herbicides, such as dinoseb, can be absorbed through the skin and are highly toxic (12). Even insect repellents such as diethyltoluanide (DEET) have the potential to be harmful (12). The potential risk to human health makes the remediation of pesticide-contaminated sites a necessary and almost urgent undertaking.

PESTICIDE SITES

Despite regulations to protect human health and the environment, many agrochemical facilities, including pesticide manufacturing and storage sites, have become Superfund sites. A list of pesticides that are found at remediation sites that will be discussed in this report is given in Table 1. A number of the pesticides listed in Table 1 have been banned, cancelled or severely restricted. Most of the pesticide-contaminated sites at one time dealt with these older persistent pesticides that are no longer used or used in a very limited manner. Improper storage and handling, particularly of pesticide wastes, has led to the contamination that we now see at these sites.

Table 1: Pesticides found at bioremediation and phytoremediation sites discussed in this report

	Atrazine	Chlordane	DDT	Dieldrin	Dinoseb	Endosulfan	Heptachlor	Lindane	Malathion	Metolachlor	Parathion	Toxaphene	Other Pesticides
Aberdeen Pesticide Dumps*			X										X
Andrews Env. Eng. Sites*	X												X
Baird and McGuire		X											X
Bower's Field*		X	X		X	X			X		X		
Ciba-Geigy Corp.			X					X					X
Charleston, SC			X									X	
Gila Indian Reservation											X	X	
Helena Chemical Co.		X	X				X					X	X
Navajo Dip Vats*												X	
Novartis Site*	X									X			
SMC Bucks, AL													X
SMC Tampa, FL*		X	X	X		X	X					X	X

*Indicates that a case study for this site has been included in Appendix A of this report.
SMC = Stauffer Management Company

In 1980, Congress passed the Comprehensive Environmental Response, Compensation, and Liability Act, which authorizes a special tax, that funds the Superfund. Superfund finances the cleanup of hazardous waste sites on the National Priority List (NPL). National Priority List sites

present the most serious threat to human health and environmental well-being. In the EPA's Superfund database, there are 1,354 sites listed, 363 of which report pesticides as a contaminant (15). Many of these sites are not specific about the pesticide contamination present. However, the list does include 13 pesticide manufacturing sites, 20 pesticide formulation sites and nine other sites, including storage facilities and aerial application facilities (15). Due to the complexity of these sites it is difficult to make generalizations regarding the types of contamination present and the remediation activities that were chosen. Table 1 presents a few select sites from this list where bioremediation has been identified as a component of the remediation process. The table also refers to several other pesticides sites where bioremediation was chosen as a remediation option. These sites will be discussed later in the paper.

The EPA's Office of Solid Waste and Emergency Response hosts an online database, know as REACH IT, which is dedicated to innovative remediation and characterization technologies. REACH IT stands for Research and Characterization and Innovative Technologies, and the website is *www.epareachit.org*. Information for this database is supplied by government officials and vendors themselves. Table 2 displays the technologies and vendors that resulted from four different searches for information regarding the bioremediation of pesticides. Phytoremediation technologies are classified as "Bioremediation - other". Search results provide information regarding the technology vendors, the sites where they have conducted cleanup projects ranging from bench scale to full scale. It also yields information on the technologies that have been developed by the vendors. The information is provided by the vendors themselves and the EPA does not check them for accuracy, nor does it actively update the database. That is all the responsibility of the vendor. The search also yields information on sites where the EPA has conducted remedial activities. Often the EPA sites are Superfund remedial sites. Many of the sites listed were not actually pesticide-contaminated sites. After reviewing the projects that were identified by the search engine, 13% of the 189 projects were actually contaminated by pesticides. More information on this database is provided in Appendix B, the annotated bibliography.

Table 2: Results of a search of *www.epareachit.org* for remediation technologies, vendors, and sites using various search criteria.

Search Criteria	Technologies	Vendors
Bioremediation	321	171
Organic Pesticides/ Herbicides	138	88
Full Scale - Organic Pesticides/Herbicides	127	80
Full-scale Bioremediation - Organic Pesticide/Herbicides	40	68

A study conducted by the Wisconsin Department of Agriculture randomly investigated 27 agriculture application businesses and found that 93% had pesticide-contaminated soils (16). Of the 27 sites, 59% had at least one pesticide present in the soil at concentrations above five parts per million (ppm) (16). At least half of the sites had pesticides in the groundwater and at least a third exceeded groundwater standards (16).

REMEDIATION OPTIONS

Evaluating Remediation Strategies

Much consideration and research needs to go into the decision making process for an effective clean up of a particular site. The chosen method must remediate the site to meet regulatory requirements. Remedial project managers need to consider the contaminants present at the site and the media in which they exist. Quite often, multiple contaminants and types of media need to be treated. The contaminants can vary widely, especially if the site is a former manufacturing facility where finished products, byproducts, raw materials and solvents can all be found together. The pollutants may be found in the soil, sediments, sludges, ground water or surface water. Ideally, treatment will result in the destruction of the compound without the generation of intermediates. Some technologies are only capable of relocating or stabilizing a contaminant and do not result in destruction. Each technology has its advantages and limitations for the treatment of specific contaminants and media. A summary of several different technologies available for the treatment of pesticide-contaminated sites is shown in Table 3.

Table 3: Comparison of available technologies for the treatment of sites contaminated by pesticides

Technology	Cost Range (per yd^3)[1]	Treatment Time (months)[2]	Treatable Media [1]	Removal Efficiency [1]	Source(s)
Low Temperature Thermal Desorption	$100 to $400	0.75	Soil, Sludge and Sediment	82% to >98%	17, 3
Incineration	$300 to $1000	1	Soil, Sludge and Sediment	Generally >99.99%	3
Bioremediation	$8.4 to $197	3.1(*ex situ*)	Soil, Sludge, Sediment and Groundwater	up to 99.8%	18, 19, 20, 6, 21, 22
Phytoremediation	~$80 or $60k to $100k/acre	No data	Soil, Sludge, Sediment and Groundwater	up to >80%	23, 20, 24

[1] Based on the treatment of pesticide contaminated media
[2] Based on treatment of 1,000yd^3 of contaminated soil contaminated with various organic compounds (25)

It is not uncommon to find a site where a combination of groundwater, soils, sediments, sludges or surface water are contaminated with pesticides. This often requires taking a different approach for each contaminated medium. For example, at a Stauffer Management Company (SMC) site in Bucks, AL contamination has been found in the soil, groundwater, ponds, swamp, sediment, fish and sludges. The contamination is not limited to pesticides either. The groundwater is being treated using a pump and treat method. Two of the solid waste units have been capped, a third requires no further action and the fourth will be treated using bioremediation. Portions of the contaminated swamp are being excavated.

Cost is generally an important factor when a method is being considered to remediate a site. The cost of remediation is generally higher per cubic yard for sites with less contaminated material. This is because of fixed costs, such as permitting and engineering site assessment costs. Each site is unique and costs are site specific. The cost estimates given in this report were calculated and gathered using the best available data but are not meant to be ironclad values. Due to the limited information available on phytoremediation demonstrations, the phytoremediation cost estimates vary widely and are not necessarily based upon pesticide remediation projects.

Taking all factors into consideration, bioremediation or phytoremediation may not be the best choice for all sites. A presentation at the 1996 Air and Waste Management Association Annual Meeting discussed the results of a treatability study for pesticide-contaminated soil, which addressed six technologies including two bioremediation approaches (25). Thermal desorption proved to be over 99% effective at removing the contaminants. The estimated cost for this treatment was between $155 and $205 per ton (25). Bioremediation using white-rot fungi was not shown to be effective at removing the DDT and toxaphene in the soil (25). Bioremediation using an aerobic/anaerobic cycling system demonstrated the capability to destroy DDT and toxaphene from the soil (25). The cost of this process was estimated to range between $80 and $120 per ton (25). Each of these three technologies will be addressed in more detail later in this paper. The results of this study show that there are trade-offs for each technology. For example, although bioremediation using aerobic and anaerobic cycling was the least expensive technology studied, it required a considerably longer time to remediate the same volume and concentration of contaminant than did thermal desorption.

The following subsections discuss two commonly employed and proven methods for the remediation of pesticide-contaminated soil in addition to innovative methods for the application of bioremediation and phytoremediation.

Low Temperature Thermal Desorption

Low Temperature Thermal Desorption is an *ex situ* clean up technology, frequently used to remediate pesticide-contaminated sites. Although it is not an innovative technology, its frequency of use merits a short discussion. It is capable of removing semi-volatile and volatile organic compounds, including pesticides, from soils and it is believed to be capable of removing pesticides from sludge, sediments and filter cakes (17). The media is heated to between 300 and 1000°F, which results in the volatilization, but not the destruction of organic compounds (17). The resulting organics in the contaminated gas stream are treated by either passing through an afterburner or condenser or they are captured by carbon adsorption beds (17). By treating the gas stream with an afterburner, the contaminants are completely destroyed. The condenser converts the gas into a liquid phase for further treatment while the carbon adsorption beds immobilize, but do not destroy the contaminants (17). Low temperature thermal desorption requires highly specialized facilities and carries a comparatively high cost. This technology is not capable of remediating inorganics or heavy metals and is limited to contaminated media that is at least 20% solids (17).

Incineration

Incineration is also a proven technology that has frequently been used to remediate pesticide-contaminated sites (3). This technology is best suited for soil, sludge or sediments with organic contaminants (3). Heat and oxygen are applied to the contaminated media and the organic compounds are subsequently oxidized (3). The first stage of incineration heats the contaminated media at temperatures between 1,000 and 1,800°F and results in some oxidation and the volatilization of the organics (3). The second stage operates at temperatures between 1,600 and 2,200°F and results in the complete destruction of organics (3). The resulting ash can be disposed of in a landfill if it meets safety regulations. Incineration has the advantage of nearly complete destruction of contaminants. It has the limitation of having high costs and a need for specialized facilities. Small quantities of contaminated media can be treated off-site at centralized facilities but transporting contaminated and hazardous material increases the liability. Some vendors have portable incinerators that may be set up on site, but often the contaminated media must be removed from the site and then transported to an incineration facility.

Bioremediation

Introduction. Bioremediation is an innovative technology that is frequently being chosen for the cleanup of sites on the National Priority List (NPL). Recent research is expanding the capabilities of this technology, which, along with its generally lower cost, has led to bioremediation becoming an increasingly attractive cleanup technology. According to the 1997 Treatment Technologies for Site Cleanup annual status report by the U.S. EPA, 11% of all treatment projects completed (excluding groundwater projects) involved some form of bioremediation (26). Numerous bench-scale and small-scale field studies have been completed and many more are in progress. Several case studies are presented in Appendix A. For a brief summary of select bench-scale bioremediation projects refer to Appendices B and C.

The process of bioremediation enhances the rate of the natural microbial degradation of contaminants by supplementing these microorganisms with nutrients, carbon sources or electron donors. This can be done by using indigenous microorganisms or by adding an enriched culture of microorganisms that have specific characteristics that allow them to degrade the desired contaminant at a quicker rate. Ideally, bioremediation results in the complete mineralization of contaminants to H_2O and CO_2 without the build up of intermediates. Bioremediation processes can be broadly categorized into two groups: *ex situ* and *in situ*. *Ex situ* bioremediation technologies include bioreactors, biofilters, land farming and some composting methods. *In situ* bioremediation technologies include bioventing, biosparging, biostimulation, liquid delivery systems and some composting methods. *In situ* treatments tend to be more attractive to vendors and responsible parties because they require less equipment, generally have a lower cost and generate less disturbance to the environment. However, the difficulties associated with implementing *in situ* processes have limited their application in the field. Bioremediation using white-rot fungi to innoculate contaminated media is a promising technology that is currently being researched. This technology can be used in an *ex situ* or *in situ* manner. Generally, this fungi is used to innoculate a composting process, but it does have other bioremediation applications.

Application. Bioreactors function in a manner that is similar to sewage treatment plants. There are many ways a bioreactor can be designed, but most are a modification of one of two systems. In the first system, which is often referred to as a trickling filter or fixed media system, the aqueous waste stream is allowed to trickle over a solid support, such as rocks, that have been colonized extensively by microorganisms. As the liquid waste stream passes over the solids, the microorganisms break down the contaminants. Before the treated waste stream can be discharged, it must be clarified so that the number of microorganisms present in the discharge meets regulations. This system can also be referred to as a biofilter, which is also used to treat contaminated gas streams. For this form of treatment to be effective, the contaminant must be volatile.

The second common bioreactor design uses a sealed vessel to mix the contaminants, amendments and microorganisms. A sealed system allows greater control over factors such as pH and O_2. The waste is pumped into the vessel where it mixes with nutrients and microorganisms. The tank is often aerated, although the process can be kept anaerobic. Often multiple bioreactors are used together to enhance the rate and extent of bioremediation. This system also requires the treatment of the waste stream to remove high numbers of microorganisms before discharge. Bioreactors, such as this, are often used to treat contaminated solids, which is referred to as slurry-phase treatment. In these systems, water is added to the soil and the slurry is continuously mixed. Amendments, such as nutrients, can be added to this system and treatment can be done under aerobic or anaerobic conditions. The SABRE™ process, which was used in the Bowers Field demonstration used a slurry-phase bioreactor based on this design to remediate herbicide contaminated soil. There are many variations of these basic designs that have been applied for the treatment of pesticides and other hazardous wastes.

Variations of either of these two systems are suitable for the treatment of contaminated groundwater. Conventional pump and treat systems are used to remove the contaminated groundwater from the aquifer. The contaminated water is then treated using either type of bioreactor. The water is then discharged in an appropriate manner. In a liquid delivery system, water is injected into the groundwater through an injection well. This water has been amended with nutrients and electron donors in order to facilitate increased *in situ* breakdown of the contaminants by indigenous microorganisms. An air pump is often used to provide oxygen and aerobic conditions. The groundwater that is produced by this process is extracted and treated if necessary. The extracted groundwater is then either disposed of or amended with nutrients and returned to the contaminated groundwater. The process continues until the extracted groundwater meets cleanup guidelines. Recirculating wells extract the groundwater, amend it and reinject it without treating it. A schematic for a process where the groundwater is amended and returned for *in situ* treatment is shown in Figure 1.

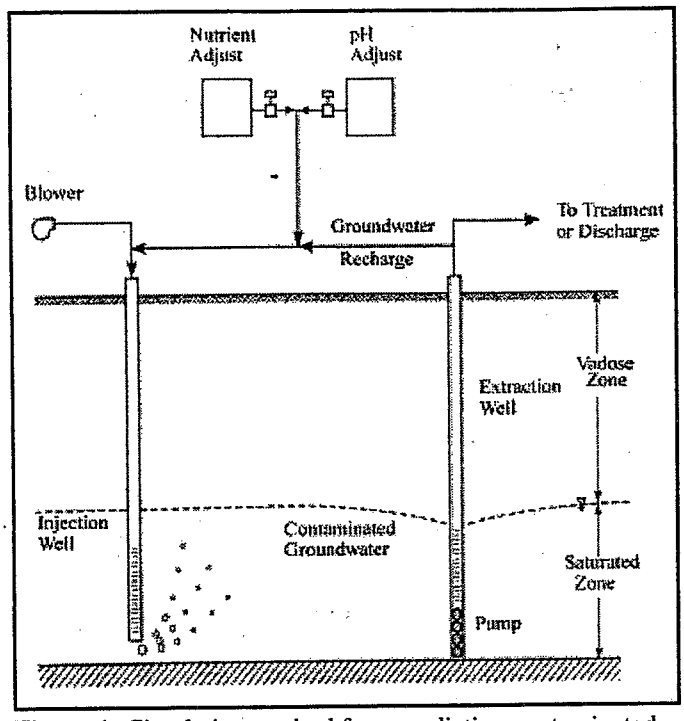

Figure 1: Circulation method for remediating contaminated groundwater (3).

Composting involves the mixing of the contaminated soil in a pile with a solid organic substrate, which serves as a carbon source for the indigenous aerobic soil microorganisms. Composting is a means for the remediation of pesticide-contaminated sites and several large companies, such as W.R. Grace and Astra Zeneca, have developed and patented successful composting technologies. For *ex situ* treatment, the soil is excavated, screened and formed into windrows or some form of pile. *In situ* treatment is also possible for composting but is not used as frequently. The soil is then supplemented with the organic substrates, nitrogen and phosphorous. Moisture, pH and redox potential are monitored while the soil is mixed on a regular basis to maintain homogeny and aeration. The piles may also be kept anaerobic by covering them with plastic sheets and encouraging the aerobic microorganisms to utilize all of the oxygen remaining underneath. Once the oxygen in the pile has been depleted, anaerobic microorganisms will become active, degrading the organic pollutants that were non-degraded by the aerobic microbial population. Figure 2 shows an aerobic windrow composting system.

The terms land farming, land spreading, land application and land treatment are often used interchangeably to refer to the same process. It is a full-scale bioremediation technology where contaminated solid media, such as soil, sludge or sediment, are applied to uncontaminated soil. Mixing of the contaminated media with the soil allows the indigenous microorganisms to interact with the contaminant and degrade it. The rate of application is calculated so as to avoid concentrations that would be unsafe in soil, groundwater or crops. Generally, the rate is similar to the label rate, which is the suggested rate of application of

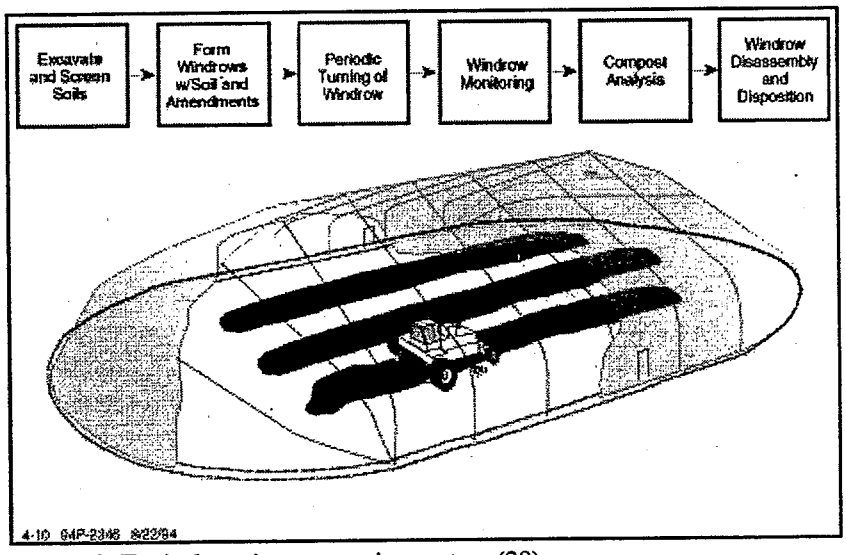

Figure 2: Typical *ex situ* composting system (28)

pesticide per unit of land or soil that is on the pesticide label. The size and location of the spreading operation is then chosen based upon the application rate. Finally, a cover crop may be added to the land farming operation. A cover crop allows a farmer to continue to use these productive fields while remediation occurs, and it may enhance rhizosphere degradation. Rhizosphere degradation will be discussed in the phytoremediation section. Often it is necessary to add nutrients in order to enhance biodegradation by these indigenous organisms. In addition, it is important to monitor soil moisture and oxygen levels. Although the land farming process is slow, it is a very low cost technology, which makes it attractive to small waste generators, such as farmers. Land spreading has been used successfully throughout the United States, particularly in the Midwest to remediate a variety of different pollutants. It is the most widely used *ex situ* bioremediation treatment process (27). Before a farmer can begin land spreading, he must obtain a permit and fully outline his intentions, including the quantity of contaminant and the soil characteristics of the land where it will be applied. When land spreading, it is required that all guidelines on the label, including rate of application and season of application be followed. The state of Wisconsin requires the oversight of the land spreading process by a certified applicator. Because pesticides reach the soil through normal application, land spreading at application rates generally doesn't require a lined bed. However, land spreading of pesticides at significantly higher concentrations or land spreading of other hazardous wastes occurs on a lined bed to collect leachate. A typical system for the land treatment of hazardous wastes is shown in Figure 3. Land spreading of some hazardous compounds can result in their volatilization, which necessitates a cap for the system to control emissions.

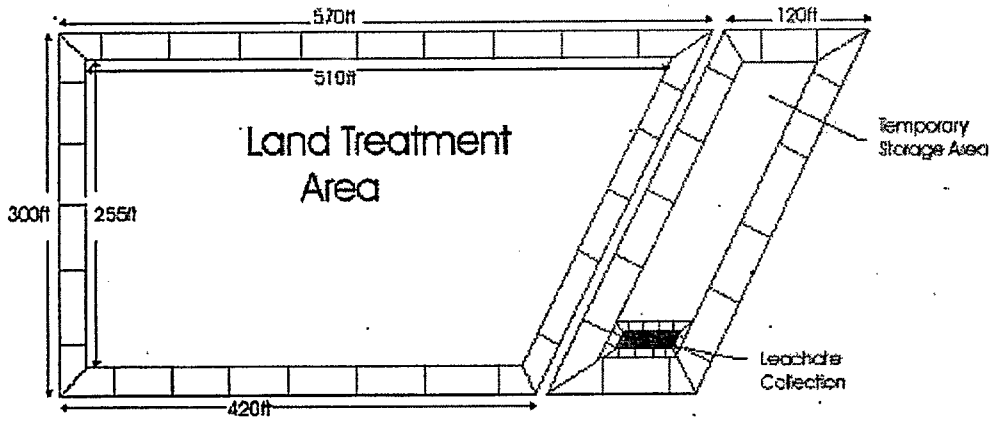

Figure 3: Typical lined-bed land treatment setup for the remediation of hazardous wastes

White-rot fungi, particularly those of the family *Phanerochaete*, are becoming recognized for their ability to efficiently biodegrade toxic contaminants. Most studies focus on the ability of *Phanerochaete chrysosporium* to degrade persistent compounds, but *Phanerochaete sordida*, *Pleuotus ostreatus*, *Phellinus weirii*, and *Polyporus versicolor* have also been successful in laboratory studies (29,30). These fungi are effective because of an extracellular enzyme that catalyzes a reaction that can degrade lignin, an aromatic plant compound. In order to catalyze these powerful reactions, the enzyme requires hydrogen peroxide which is produced by the fungus. These fungi are capable of degrading chlordane, lindane and DDT, which makes them useful for the remediation of pesticide-contaminated sites (31). White-rot fungi could be used to innoculate a composing operation. However, large quantities of the fungus are required to

remediate a site due to the very slow nature of compound degradation (29). Other studies have demonstrated the ability of white-rot fungi to degrade DDT in aqueous cultures.

Bioventing and biosparging are very similar *in situ* processes. Both methods involve the introduction of O_2 into permeable soil to increase the activity of aerobic microorganisms. Bioventing introduces the O_2 to the vadose, or unsaturated zone, while biosparging introduces O_2 below the water table into the saturated zone. Neither of these processes are suitable for compounds which may volatilize too quickly. Biosparging can force volatile contaminants out of the water table and up into the unsaturated zone, where it the vapors can be recovered Because of this, it is necessary to monitor offgases. Biosparging also introduces O_2 to the saturated zone, which will increase the rate of biodegradation. These procedures have not been used frequently with pesticide-contaminated sites.

Monitored natural attenuation is the remediation of contaminated media by indigenous microorganisms without active treatment. This remediation process requires a longer time frame to reach remediation goals than active bioremediation methods. Due to the longer time frame, a more intensive monitoring program needs to be implemented to assure that attenuation is occurring.

Bioremediation of Pesticides. The bioremediation techniques discussed above apply to a variety of contaminants. It is not always possible to use each technology with pesticide-contaminated media. This section gives a brief overview of some past, current and pending applications of bioremediation for pesticides. The case study section of this report (Appendix A) examines several well-documented full-scale and demonstration-scale bioremediation projects in greater depth. Additionally, Appendix C lists a number of small-scale bioremediation studies that have been performed and are not described in this section. It is important to note that the small-scale bioremediation studies presented in Appendix C represent only a small fraction of the studies that have been conducted by researchers at universities, private companies, and government agencies.

The Gila Indian Reservation in Arizona is the site of an abandoned airfield that was at one time used for aerial application activities (32). The project involved the treatment of about 80,000 yd^3 of soil using *in situ* land treatment in order to remove parathion and toxaphene (32). Following chemical oxidation treatment and prior to biological treatment, toxaphene was present at 1,470ppm and parathion was present at 110ppm (33). Biological treatment was conducted in an *in situ* manner. The soil was amended with water and nutrients to enhance the rate of biodegradation (32). Parathion degradation proceeded rapidly, but toxaphene was not degraded below desired cleanup levels (34). In order to promote degradation, a variety of amendments were added including alfalfa, manure, sludge, sulfuric acid and hydrogen peroxide (32). Remediation was also attempted with and without water (34). Finally, the site was capped, anaerobic conditions were established and the pH was adjusted, which promoted the biodegradation of toxaphene to acceptable levels (34).

Currently, several Superfund sites have identified bioremediation as an effective means of treating pesticide-contaminated soil and groundwater. For example, the Baird and McGuire Superfund site in Holbrook, Massachusetts, has been using bioremediation to clean pesticide-

contaminated groundwater for several years. The site was used for the production and storage of pesticides, disinfectants, soaps and solvents beginning in 1912 (35). Production wastes were stored or disposed of on site. An aerobic bioreactor was chosen to treat the contaminated groundwater. The system is capable of treating 300,000 gallons a day, and the treated water is being discharged to an on-site aquifer. The system treats an average of 21 million gallons a year at a cost of $2 million a year. A Ciba-Geigy Corporation-owned pesticide manufacturing facility in McIntosh, Alabama, has approached the long-term cleanup of groundwater contaminated by DDT, lindane and other pesticides using a similar system. The groundwater is being pumped to an on-site biological treatment system and then discharged to a local river (15).

Table 4 presents a number of sites where bioremediation or phytoremediation have been selected as the remedy. The table indicates the particular treatment method along with the contaminated media. The remediation projects listed in Table 4 are either demonstrations or Superfund sites. The number of these projects is small and the majority are described in this table. Many projects are currently operating, which makes it difficult to draw conclusions regarding the duration of these projects and to comment on the cost and performance of the treatment method.

Table 4: Bioremediation and Phytoremediation implementation at several pesticide-contaminated sites.

Site Name		Treatment Method	Commercial Technology	Contaminated Media
Aberdeen Pesticide Dumps*	S	Phytoremediation•	N/A	Groundwater and soil
Baird and McGuire	S	Pump and Treat	N/A	Groundwater, soil and sediment
Bowers Field*	D	Bioreactor	SABRE	Soil
Ciba-Geigy Corp.	S	Pump and Treat, *in situ* bioremediation	N/A	Groundwater, soil, surface water, sediment and sludges
Charleston, SC	D	Composting•	DARAMEND	Soil
Gila Indian Reservation	S	Composting•	N/A	Soil
Helena Chemical Co.	S	Composting	XENOREM	Soil
Navajo Dip Vats*	S	Bioreactor	N/A	Soil
Novartis*	D	Composting	DARAMEND	Soil
SMC Bucks, AL	S	In design process		Groundwater, soil, sediment, sludges and wetlands.
SMC Tampa, FL*	D	Composting	XENOREM	Groundwater, soil, surface water and sediment

*Indicates Case Study is available in Appendix A
(S) indicates Superfund project, (D) indicates technology demonstration.
•Indicates *in situ* treatment process
Underlined media represents the media treated through bioremediation or phytoremediation

Based on the information from these sites, a few generalizations can be made regarding which technologies have seen the most use or success for the remediation of a particular class of

pesticides. The organophosphate pesticides, including malathion and parathion appear to be best degraded by aerobic treatment such as composting and land spreading. Groundwater containing organophosphates has been successfully remediated in several pilot and bench studies using aerobic bioreactors. The organochloride pesticides, including chlordane, DDT and toxaphene appear to require a cycling of aerobic and anaerobic phase in order for remediation to be most successful. The anaerobic phase reductively dechlorinates these pesticides while the aerobic phase completes the mineralization of the compound. White-rot fungi have also shown to be promising in the remediation of organochlorides. Metolachlor and the triazine pesticides appear to degrade significantly under land spreading and composting conditions.

Limitations. Although bioremediation appears to be a promising alternative for the remediation of pesticide-contaminated sites, it is still in the developmental phase. Many bench-scale projects are being conducted to optimize bioremediation protocols and to expand the number of compounds for which bioremediation is feasible. In 1996, bioremediation failed to clean up contaminants at a former pesticide formulation factory (36). Of the seven pesticides present, only one, chlordane, saw significant reductions but still did not meet regulatory goals. The soil was subsequently treated by incineration. At a second Superfund site in Leetown, WV, treatability studies showed that bioremediation would not be able to meet the necessary standards. Upon re-evaluation of this pesticide disposal facility, it was determined that the site did not pose an unacceptable risk and no further remedial action was taken.

Phanerochaete chrysosporium and *Phanerochaete sordida* were investigated by a group of researchers to determine their ability to degrade DDT contaminated soil from a former pesticide production plant using a land farming approach (30). Despite vigorous growth, both of these white-rot fungi were unable to remediate the soil under laboratory conditions (30). Other studies have shown DDT degradation by white-rot fungi but not extensive mineralization (37,29). Generally, most DDT is transformed to DDD or DDE. These results indicate that more research is necessary before white-rot fungi can be used on a regular basis to remediate pesticide-contaminated sites.

Research and technology development have found ways to stimulate biological activity and thus decrease the length of time that treatment requires. In general, bioremediation treatment still tends to require more time than thermal treatment. Due to its innovative nature, the immense number of microorganisms known and the vast number of problematic compounds, bioremediation is a research intensive technology. Research is ongoing in its efforts to reduce the current limitations to bioremediation. Before any full-scale bioremediation project can begin, treatability studies must be conducted. Once remediation is under way, routine monitoring must be conducted. This can increase the time that it takes to initiate site clean up and it can raise the costs. Byproducts of contaminant transformation are sometimes hard to predict. In the case of some chemicals, such as DDT, degradation leads to formation of the toxic byproducts, DDD and DDE. Even if the microorganisms are capable of detoxifying or metabolizing a compound, very high concentrations of contaminants can be toxic to them. Finally, those compounds that resist biodegradation, or recalcitrant compounds, are often not capable of efficient treatment using bioremediation and an alternative must be found.

Phytoremediation

Introduction. Phytoremediation is also an innovative technology that is gaining recognition as a cost-effective and aesthetically-pleasing method of remediating contaminated sites. Due to the fact that herbicides are designed to kill plants, the use of phytoremediation to remediate them can be a difficult and complicated task. Many studies have been done to determine the effectiveness of remediating persistent pollutants with various plant species (see Appendix C) and more results are frequently being reported. The projects described in Appendix C represent only a small fraction of the total number of phytoremediation projects in this area.

Application. A significant amount of work has been conducted to examine the ability of plants to remediate heavy metal contaminated soils. Plants are often capable of the uptake and storage of significant concentrations of some heavy metals and other compounds in their roots, shoots and leaves, referred to as phytoextraction. The plants are then harvested and disposed of in an approved manner, such as in a hazardous waste landfill. This technique results in up to a 95% reduction in waste volume over the equivalent concentration of contaminated soil. The plants that are capable of this type of remediation are referred to as hyperaccumulators. Types of plants that appear promising for this form of remediation include the mustard plant, alpine pennycress, broccoli and cabbage (38).

Phytotransformation occurs when plants transform organic contaminants into less toxic, less mobile or more stable form. This process includes phytodegradation, which is the metabolism of the organic contaminant by the plant enzymes and phytovolatilization, which is the volatilization of organic contaminants as they pass through the plant leaves. The release of these pollutants into the air results in the exchange of one form of pollution for another.

Phytostabilization immobilizes the contaminants and reduces their migration through the soil by absorbing and binding leachable constituents to the plant structure. This process effectively reduces the bioavailability of the harmful contaminants. Almost any vegetation present at contaminated sites will contribute to phytostabilization (38).

At the soil-root interface, known as the rhizosphere, there is a very large and very active microbial population. Often the plant and microbial populations provide needed organic and inorganic compounds for one another. The rhizosphere environment is high in microbial abundance and rich in microbial metabolic activity, which has the potential to enhance the rate of biodegradation of contaminants by the microorganisms. Generally, the plant is not directly involved in the biodegradation process. It serves as a catalyst for increasing microbial growth and activity, which subsequently increases the biodegradation potential. However, the rhizosphere can be limited in its remediation potential because it does not extend far from the root. This process is often referred to as phytostimulation or plant-assisted bioremediation.

Phytoremediation of Pesticides. Currently, a significant amount of research is being conducted on the interaction between microorganisms and plants in the rhizosphere and the potential to use this for the remediation of pesticide-contaminated media. According to preliminary studies, enhanced degradation of atrazine, metolachlor and trifluralin have been observed in contaminated soils where plants of the *Kochia* sp. have been planted (39). The increased

degradation occurs in the rhizosphere of this herbicide-tolerant plant, suggesting that rhizosphere interactions between the plant and microorganisms have led to the increased degradation of the pesticides present (39). Additional studies using the *Kochia* sp. have been conducted by these researchers and also show promise for the phytoremediation of pesticide-contaminated soils and groundwater (38).

In laboratory studies, the quick-growing and deep-rooted poplar tree has been shown to be successful in the remediation of groundwater (40). Its rapid growth requires high volumes of water, that are pulled from the saturated zone. Contaminated groundwater is absorbed by the plant and the pollutants are subsequently transformed into organic molecules for plant growth. This technique has already proven successful for the remediation of atrazine-contaminated soil and groundwater (40). Hybrid poplars are being used in the remediation of a farm chemical site with high levels of nitrate, atrazine and arochlor in the groundwater (41). Approximately 1.5 acres are being treated and results to date show reduction of both the nitrates and herbicides in the groundwater (41).

Limitations. Phytoremediation is not the answer to all contamination problems. Plants can generally only remediate soil or sediment in the top three feet of the soil because of their root lengths. Phytoremediation is generally limited to a depth of ten feet for groundwater remediation. As with bioremediation, phytoremediation is a research-intensive technology, and it can require long periods of time to effectively remediate a site. Plants that take up the contaminants from the soil and transport them to their stems or leaves without biodegrading them to non-toxic compounds could potentially harm herbivores (38). Phytoextraction and phytostabilization do not actually result in the destruction of the contaminant. Instead they accumulate or immobilize the contaminant. Although these are beneficial outcomes, destruction of the contaminant is generally preferred. Phytoremediation is still relatively unproven and its capabilities are still being discovered.

CONCLUSIONS AND RECOMMENDATIONS

Persistent organic pollutants are becoming an increasing global concern. Developed nations have the capacity to find alternatives and treatments for these harmful pollutants. Developing nations still rely on these chemicals and require assistance to implement alternatives to clean up the contamination that these chemicals have caused. Those pesticides identified by the proposed UN treaty are not the only ones of concern. The triazine and organophosphate pesticides are also capable of persisting in the environment and causing concerns for human health.

Remediation projects have been conducted at numerous pesticide-contaminated sites. Incineration and low temperature thermal desorption are proven and frequently used methods for the remediation of these sites, while bioremediation and phytoremediation are innovative alternatives that are gaining support. Many remedial project managers are looking for low cost options such as bioremediation and phytoremediation. Full-scale demonstrations and remedial actions, such as those discussed in the body and Appendix A of this report, show that bioremediation can be used successfully. Many of the technologies developed and employed at these sites are now being considered or used to remediate additional sites.

Because of the conditions that vary between each contaminated site, bioremediation and phytoremediation are not feasible in every case. Before a remediation project can begin, all of the site-specific factors must be taken into account, and a decision must be made based upon the most suitable available technology. Many research groups are conducting laboratory and pilot-scale bioremediation and phytoremediation projects on pesticides, which promise to increase our knowledge of the applications and limitations of these innovative technologies. Programs such as the Superfund Innovative Technology Evaluation (SITE) and the Federal Remediation Technologies Roundtable will continue to promote these innovative strategies. With time and increasing numbers of successful implementations, bioremediation and phytoremediation will be considered proven technologies, rather than innovative technologies.

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Appendix A: Case Studies

Bioremediation

In recent years a number of extensive and successful full-scale bioremediation projects and large scale demonstration projects have been conducted. Most of these projects have been well documented and provide a wealth of information regarding the general status of bioremediation technology and potential remediation options. Despite the increasing number of these projects, the information is still limited.

Bowers Field - SABRE™ Technology

The Bowers Field site is a county-owned airport in Ellensburg, WA. The pesticide of concern at Bowers Field is 2-sec-butyl-4,6-dinitrophenol, commonly known as dinoseb, which is an herbicide. Dinoseb accumulated at the airfield as a result of aerial application activities and has persisted and remained at the site since the chemical was banned in 1986. Prior to treatment, dinoseb concentrations averaged 27.3 mg/kg and ranged from 14 to 34 mg/kg (18). Although the remediation effort focused on dinoseb, other pesticides were present at parts per million concentrations prior to treatment. Due to dinoseb's persistent nature, sites contaminated with it and other chemically similar compounds have generally been treated by incineration.

The SABRE™ (Simplot Anaerobic Biological Remediation) process was developed by the University of Idaho and the J.R. Simplot Company. This technology is capable of biodegrading nitroaromatic compounds, such as TNT and dinoseb. Under aerobic conditions dinoseb undergoes oxidation and is transformed to its amino and acetamido forms, which are also toxic (42, 43). These compounds can then form polymers, which can be used by microorganisms to form other toxic compounds (43). Therefore, it is desirable to avoid aerobic transformation of these compounds. The SABRE™ process uses microorganisms in an anaerobic environment to enzymatically attack nitroaromatics in the soil and biodegrade them into acetate and organic acids. The J.R. Simplot Company conducted a demonstration of their SABRE™ process at the Bowers field site during the summer of 1993 through the U.S. EPA's Superfund Innovative Technology Evaluation (SITE) program (18). A second demonstration of this technology was also conducted at Weldon Spring Ordnance Works on TNT, also supported by the SITE program.

For the Bowers field demonstration, untreated soil was excavated from the contaminated site and passed through a vibrating screen in order to remove rocks and debris that were greater than 12.7mm in diameter (18). Dinoseb is water soluble, therefore the large rocks and debris were washed with water in order to remove the dinoseb from them. The rinse water was added to uncontaminated "make-up" water in order to achieve a final concentration of one liter of water per kilogram of soil. A total of $30m^3$ of untreated soil, followed by 30L of water was transferred to a single portable bioreactor (18). Larger scale remediation projects using the SABRE process can use lined pits or larger modular bioreactors. In addition to the soil and water, phosphate was also added as a buffer to keep the pH close to neutral over the course of the treatment (18). The flow diagram in Figure A-1 outlines the process for treating contaminated soil with the SABRE™ technology.

The SABRE™ process functions by augmenting contaminated soil with naturally selected microorganisms in an anaerobic environment. Prior to treatment of the contaminated site, a soil sample is taken and brought back to the lab. In the lab, researchers culture the microorganisms and select species capable of biodegrading dinoseb. By augmenting the contaminated soil with these enriched cultures, it is possible to increase the rate of dinoseb degradation. For this demonstration, $0.02m^3$ of previously treated soil, which contained a sufficient quantity of enriched microorganisms, was added to the untreated soil in the bioreactor (18). Research has shown that nitroaromatic compounds, such as dinoseb, will not degrade under aerobic or microaerophilic conditions (42). In order to create an anaerobic environment a starch substrate is added. The starch substrate is a byproduct "centrifuge cake" from a potato processing plant in Idaho, which is also owned by the J.R. Simplot Company. The starch substrate contains 42% solids, 215 mg/g available starch, 6.7 mg/g total nitrogen, 2.6×10^4 culturable heterotrophic bacteria/g and 8×10^3 culturable amylolytic bacteria/g (43). The final volume of soil, water and starch substrate filled 75% of the portable bioreactor (18). The bioreactor also contained a mixer at each end that rotated at 37 rpm. In order to avoid "dead spots," the reactor was also equipped with a lancer, which pumped the settled sediment towards the mixers at the ends.

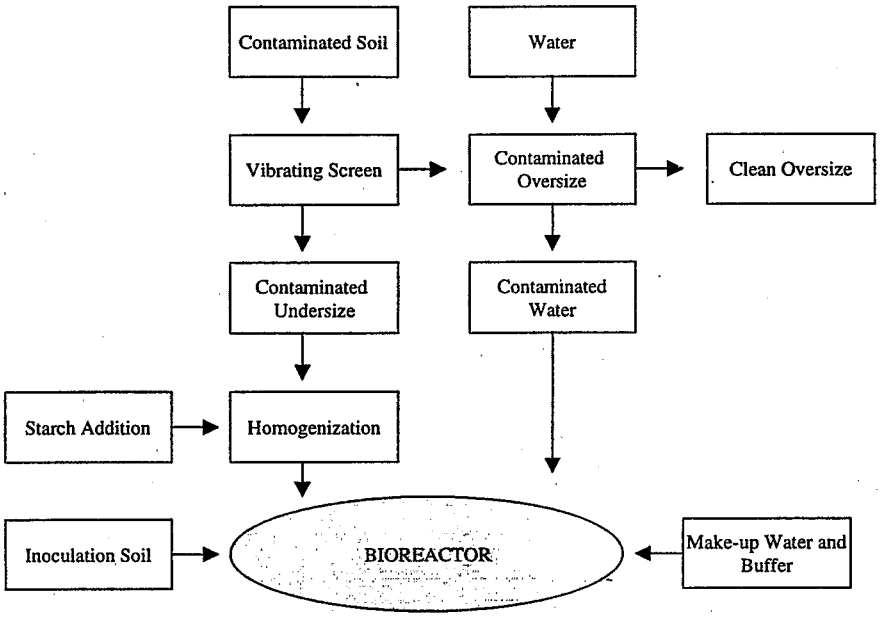

Figure A-1: Flow diagram for the SABRE™ process for the bioremediation of contaminated soil (adapted from 24, 28)

The starch degrading microorganisms breakdown the starch and consume oxygen, which subsequently creates an anaerobic environment. Anaerobicity is measured by redox potential that was monitored throughout the treatment. The redox potential reached negative 200mV, which indicates anaerobic conditions, within the first three days (18). Temperature and pH were also monitored throughout the treatment. The optimum temperature range for treatment is between 35 and 37°C and the optimum pH range is between 7 and 7.5 (18). Readings were taken and recorded every 15 seconds by a data logger.

Despite less than optimum temperatures, the treatment process lasted only 23 days. The average temperature during treatment was 18°C (18). By the end of the treatment, dinoseb concentrations were below the analytical detection limit, which corresponds to a removal efficiency greater than 99.8% (18). The detection limit for dinoseb in the soil is 0.03mg/kg. No known intermediates were detected during the analysis. The control soil had a 26.8% reduction in dinoseb over the same period of time (18). In addition to dinoseb it was also noticed that

nitroanaline was reduced by the treatment to levels below the detection limit of 0.75mg/kg, which corresponds to a greater than 88.6% removal efficiency (18). Prior to treatment, malathion, parathion and 4,4'-DDT were all detected in the soil in parts per million concentrations but were not the focus of the remediation process. Following treatment, concentrations of each of these pesticides were reduced below detection limits (18). Atrazine, chlordane and endosulfan were also detected in the contaminated soil but not considered during treatment. They were not affected at all by the treatment process. The heavy metals found in this soil were not believed to have been effected by this process and subsequently were not analyzed. Following the analysis of the treated soil, J.R. Simplot gained permission to return the soil to the site because it no longer posed a threat to the environment or human health (18). Water from the bioreactor was discharged to the sewer.

Based on the Bowers Field demonstration J.R. Simplot estimated the cost of remediation using the SABRE™ process to be $97/yd^3 for a treatment volume of 5,000 yd^3 of soil (18). This estimate does not include the cost of soil excavation. As with all remediation projects the cost is highly site specific. This estimate is based upon treating 5,000 yd^3 of contaminated soil that has similar characteristics to the soil at the Bowers field site in four lined pits for 30 days (18). Variations from this process, such as the use of modular bioreactors instead of a lined pit, could increase the cost by an additional $100/yd^3 (18). More recent cost reports indicate that this technology can remediate a dinoseb contaminated site of almost any size at costs approaching $100/yd^3 (44). The costs of remediating a TNT contaminated site, using this same technology would cost approximately $120/yd^3 (44).

Following this demonstration the SABRE™ license was transferred to the University of Idaho due to a change in business direction by J.R. Simplot. The remainder of the site was not treated due to financial restrictions of the state and county (44). Currently, the University of Idaho licences the technology on a site by site basis to individual contractors. A Washington state based contractor has applied to use this technology to remediate a dinoseb contaminated farm site outside of Grandview, WA (44). Despite the fact that dinoseb can not be remediated using low temperature thermal desorption, it was initially chosen as the method for remediating this site. When low temperature thermal desorption failed, it was necessary to haul away the hazardous material to a landfill at a high cost (44). Since then groundwater contamination and additional soil contamination have been identified and both will be treated using the SABRE™ process (44). The groundwater will be treated by pumping it to a biofilter system, which will employ the SABRE™ process.

The SABRE™ technology was also used to successfully remediate a dinoseb contaminated site in Reedley, CA in 1994. This demonstration was conducted under the California Technology Certification Program and resulted in a decrease in dinoseb concentrations from greater than 600 ppm to below detection limits (45). This successful demonstration led to the use of the SABRE™ process for full-scale remediation of the site. The full-scale treatment remediate 270yd^3 in 35 days (45).

Novartis Site - Daramend™ Technology

The Novartis site in Cambridge, Ontario was used as a warehouse and pesticide formulation facility beginning in 1972 (6). The contaminant of concern at this site is metolachlor, which is a chlorinated herbicide. Prior to treatment the concentration of metolachlor was 170 mg/kg (6). Other tests of the contaminated soil showed that concentrations of 2,4-D and atrazine were also present at the site (6). During this demonstration 200 tons of contaminated soil were treated over an 18 month period. This technology demonstration was also a part of the US EPA's SITE program.

The Daramend™ process was developed by the W.R. Grace Company and is a composting process that cycles between aerobic and anaerobic conditions. Under anaerobic conditions indigenous microorganisms are capable of partially transforming the pollutant through reductive dechlorination, results in the replacement of chlorine atoms on the hazardous compound with hydrogen atoms. Over a very long period of time these microorganisms would completely mineralize the pollutant, but by introducing oxygen and creating aerobic conditions, the mineralization occurs much more rapidly. Unfortunately, the microorganisms that operate under aerobic conditions are not capable of catalyzing the first step. Therefore it is necessary to cycle the contaminated soil between anaerobic and aerobic conditions.

The demonstration at the Novartis site was conducted between March 1996 and September 1997. Three plots were designed to test the effectiveness of the Daramend™ technology: Plot A was the main treatment plot, Plot B was the high metolachlor concentration test plot and Plot C was the static control plot (6). A greenhouse was constructed that covered all three treatment plots. For the anaerobic cycle, the Daramend™ amendments were mixed with the excavated soil, which was then irrigated and covered with a tarpaulin. The patented Daramend™ amendment consists of both organic and inorganic material. The organic material is fibrous and generally comes from plant matter (46). It serves as a source of organics for the aerobic microorganisms that consume oxygen, creating an anaerobic environment (46). The inorganic amendment consists of multi-valent metals that are capable of being oxidized and reduced. They serve as electron donors and acceptors for the anaerobic microorganisms (46). For the aerobic cycle during this demonstration, the tarpaulin was removed and the soil was tilled twice a week (6). The soil was hand tilled in the high Metolachlor plot, which resulted in only the top 30cm being tilled rather than the full 60cm depth (6). No amendments were added during the aerobic cycle. The treatment lasted for ten anaerobic/aerobic cycles (6).

The soil was analyzed for metolachlor using HPLC at day 0, 2, 7, 98, 208, 306, 454, and 565 of the treatment (6). On day 0 and 565 (the first and last days) the soil was also analyzed for 2,4-D, dinoseb, atrazine, chloride and selected metals. 2,4-D was reduced from an initial concentration of 3.7 mg/kg to below the analytical detection levels (6). Dinoseb was not detected at any point before, during or after the treatment (6). Atrazine was reduced from 17 mg/kg to a concentration below the detection level (6). The rate of metolachlor degradation over the course of the study is shown in Figure A-2 for the main treatment plot, the high metolachlor (HM) plot and for the control plot (6). In the main treatment plot metolachlor was reduced from a concentration of 67 mg/kg to a final concentration that was below the detection level of 1.0mg/kg, which corresponds to a greater than 98.5% removal efficiency (6). In the high metolachlor plot the initial

concentration was 170 mg/kg, which was reduced to a concentration of 38 mg/kg following treatment, equating to a removal efficiency of approximately 78% (6). However, only the top 30cm of the soil was tilled in this plot, which resulted in incomplete mixing. The average concentration of metolachlor in the top 30cm of the soil was11.8 mg/kg, which equates to a 93% removal efficiency (6). In the control plot metolachlor concentrations did not decrease.

Based upon this demonstration, Grace projects a cost of approximately US$73,000 for the remediation of the remaining 600 tons of contaminated media at the Novartis site (6). This estimate equates to approximately US$120/ton. According to Grace, a full-scale remediation of 2,500 to 5,000 tons of waste would cost approximately US$52-81/ton, depending upon site specifics (6). This technology appears promising for the remediation of both metolachlor and atrazine.

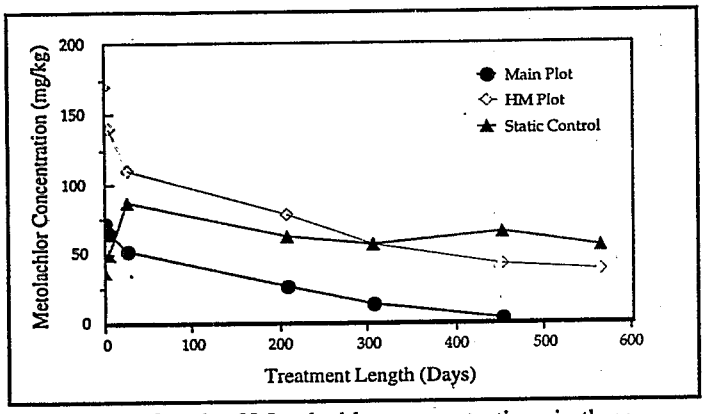

Figure A-2: Graph of Metolachlor concentrations in three treatment plots over the course of treatment (50)

Patents have been issued to W.R. Grace & CO. for the Daramend™ process and additional remediation projects are underway. This process has been used in a technology demonstration at a chemical manufacturing plant contaminated with chlorinated pesticides in Ontario, Canada (47). According to the technology developer, DDT, DDD, DDE, 2,4-D and 2,4,5-T were reduced from 250 tons of contaminated soil by 99.5% (48). At a site in Charleston, South Carolina the Daramend™ process was used successfully in an *in situ* pilot-scale demonstration to remediate toxaphene and DDT (48). According to the technology developer, toxaphene was reduced by 98% and DDT was reduced by 90% from contaminated spoil (48). Work has recently begun to remediate a toxaphene contaminated superfund site in Montgomery, AL (47).

Stauffer Chemical Company, Tampa, FL - Xenorem™ Technology

From 1953 until 1986 the Stauffer Chemical Company site located in Tampa, Florida served as a facility for the manufacture and distribution of organochloride and organophosphate pesticides. From 1953 until 1973 waste materials were disposed of on site by either burial or by small incinerator (49). Site investigations revealed that pesticides were present in soils, groundwater, surface water and pond sediments (49). Soils were tested for the presence of 32 different pesticides, several of which are classified as POPs (9). Information regarding the initial and final concentrations of select pollutants is shown in Table A-1.

Initially, low temperature thermal desorption was chosen to remediate the site at an approximate treatment cost of $130/yd^3 (50). This cost does not include setup and other infrastructure costs. However, the historic usage of this site as a pesticide manufacturing facility left a variety of compounds in the soil which made thermal desorption a difficult technology to safely implement

(50). Coupled with the need for expensive emissions treatment equipment, this raised the final cost of using low temperature thermal desorption to approximately $500/yd^3 (50).

Bioremediation using the Xenorem™ process was chosen as the means to remediate 1000yd^3 soil as technology demonstration (9,50). The Xenorem™ process was developed by Stauffer Management Company, which is a subsidiary of the Astra Zeneca Group PLC. The process involves the construction of composting windrows using contaminated soil and solid amendments. Although the process described here used three unspecified amendments, the Xenorem™ patent states that preferred amendments include agricultural wastes and municipal waste sludges (51). Typically, the amendments will also include bulking agents, such as grass, sawdust or peat (51). Surfactants may be added to the amendments in order to make the DDT more accessible to the soil microorganisms (51). Indigenous microorganisms consume the available oxygen and the pile is covered in order to create an anaerobic environment (9). Over the course of treatment moisture, organic matter, inorganic composition, and pH are all monitored (9).

Application of the Xenorem™ process at the Stauffer Chemical Company in Tampa, Florida began with the excavation and screening of the contaminated soil. The soil was then formulated into windrows inside a warehouse (9). Because of this site's proximity to residential areas it was necessary to install an odor abatement system (9). Anaerobic conditions were created by covering the pile with a tarp. Redox potential was maintained below -200mV (49). Aerobic conditions were created by removing the tarp and either mixing the soil or injecting compressed air into the pile at regular intervals (9). During the aerobic phase the redox potential was maintained above 100mV (51). At the beginning of the treatment Amendments A and B were added to the soil and comprised 40% and 5% of the total pile volume, respectively (9). At weeks 14 and 22, Amendment A was again added to the pile, but at these time points Amendment A was only 20% of the total pile volume (51). At week 33 Amendment A was added again, comprising 40% of the pile volume. Finally, in week 48 Amendments A and C were added to the pile and comprised 40% and 5% of the total pile volume, respectively (9). Prior to the addition of amendments at week 33 and at week 48 a portion of the growing pile needed to be removed due to warehouse size restrictions (9). Treatment time was approximately double that required in order to achieve cleanup goals, to allow for development of amendment evaluations and process control strategy optimization at the commercial scale (50).

The results of the treatment activities for selected contaminants are given in Table A-1. Concentrations of DDD, DDT, and toxaphene were reduced by more than 90% (9). Chlordane concentrations were reduced by slightly less than 90% (9). Toxaphene by-products present in the contaminated soil were reduced 91% by the treatment (9). Treatment brought concentrations of DDE, DDT, and dieldrin below target levels for the clean up of this site (9). Chlordane, DDD and toxaphene did not meet the remediation goal (9). The remaining contaminants listed in Table A-1 were not present in high enough concentrations to be of concern during the remediation planning (9). However, their reduction to below detection levels is a promising lead for future research. Problems with poor quality amendments and poor mixing equipment led to three of the five amendment periods operating at less than optimal levels (9). With higher quality amendments and better mixing equipment it may be possible to reduce treatment time and

increase the remediation efficiency. One drawback of this process is the high volume addition of amendments, which makes the use of a warehouse as the treatment site difficult.

Table A-1: Remediation Efficiency of Select Pollutants at the Stauffer Chemical Company Site (9)

Contaminant	Initial Conc. (mg/kg)	Final Conc. (mg/kg)	Remediation Efficiency
Chlordane	47.5	5.2	89%
DDD	242*	23.1	90.5%
DDE	11.3	6.8	40(Goal acheived)
DDT	88.4	1.2	98
Dieldrin	3.1	BDL	NA
Toxaphene	469	29	94
Aldrin	1.5	BDL	NA
Endrin	28	BDL	NA
Heptachlor	1.2	BDL	NA

NA - Not Applicable, BDL - Below Detection Limits
* Consists of original DDD and the amount converted from DDT during the first few weeks of treatment.

The estimated cost was not based upon the demonstration conducted at the Stauffer Chemical Company site. A typical cost estimate was provided by Stauffer Management Company of $192/yd^3, which covers complete project costs including the use of an environmental contractor, infrastructural and site restoration (9). The variable cost of treatment is a small fraction of this overall project cost. However, the Stauffer Chemical Company Site had higher than average costs due to its residential location and the need to tightly restrict noise and air pollution. The Xenorem™ is currently being used to remediate the remaining 16,000yd^3 of contaminated soil.

The Xenorem™ process was granted several US patents and is currently licensed to several environmental engineering firms, including one firm remediating a US Air Force base and another remediating a site in New Zealand (50). Based on the Xenorem™ technology, a bioremediation center was established, which is currently working on its first bioremediation project (50). The Xenorem™ technology is currently being used to treat contaminated soil at the Helena Chemical Company in Tampa, FL in a manner similar to the one that it used at the Stauffer Management Company site. The Helena site is a Superfund site and a former pesticide formulation plant that has been in operation since 1929 (52). The pesticides of concern at this site include aldrin, chlordane, heptachlor, dieldrin, DDT, DDD, and toxaphene, which are pesticides named on the UNEP list of POPs. Currently, this technology has achieved 70% destruction of toxaphene at this site in only six weeks.

Navajo Dip Vats

Toxaphene was used at 170 to 250 dip vat sites on the Navajo Indian Reservation in Window Rock, AZ from 1948 to 1982. Toxaphene is a chlorinated insecticide that was used to prevent ectopic parasites from infecting livestock. Concrete lined vats were positioned at and below the soil surface and filled with a toxaphene solution. A corral was generally adjacent to the vat and the livestock were driven into the vat where they were immersed in the insecticide and allowed to swim or walk out the shallow end. Each vat contained approximately 20,000 gallons of insecticide solution and was emptied and refilled daily until all livestock had been treated. This procedure was repeated once a year. Waste pesticide solution was discarded into storage ponds or simply pumped out of the vat and onto the ground. The especially dry climate in this region inhibited toxaphene breakdown or migration. Prior to treatment, toxaphene levels varied between vats, but were as high as 33,000 ppm. The dip vats were operated by the Bureau of Indian Affairs (BIA) under laws and programs for livestock grazing established by the Department of the Interior. In the late 1950s the BIA transferred responsibility for the vats to the Navajo Nation. In 1982 the EPA banned the use of toxaphene. In 1992 the Navajo Nation Superfund Office contacted EPA Region 9 regarding the site, which subsequently contacted the Environmental Emergency Response Team (ERT). ERT conducted preliminary research to determine if bioremediation would be a suitable means for treating the site. Laboratory tests showed that bioremediation was capable of degradation of up to 80% of the toxaphene (53).

The remediation site addressed by this action consists of twenty-two dip vat sites which present an immediate danger to the environment and to human health. Prior to full-scale treatment a pilot-scale study was conducted at two of the vats. Due to the distance between the dip vats, project managers realized that they would need a system that was mobile and easy to implement. Bioremediation was tested by creating slurries of the contaminated soil and amendments. The slurries were mixed and poured into 325 gallon tanks and allowed to ferment for three months (53). Once the anaerobic phase was complete, the slurry was spread over treatment beds, covered in hay and irrigated, producing the aerobic phase. The demonstration was successful and bioremediation was used to treat the remaining dip vats. However, prior to full-scale treatment several modifications were made. The results of the demonstration indicated that it was not necessary to conduct an aerobic phase (54). Therefore, the aerobic phase was not implemented in the full-scale treatment in order to save time. Due to the larger quantities of soil to be treated in the full-scale operation, tanks were too small to be used for the slurries; instead polyvinyl chloride (PVC)-lined treatment pits were used.

In 1994 the full-scale treatment process began with the excavation of the contaminated soil to a depth of four feet. The soil from these sites was transferred to a total of 45 treatment pits. Prior to adding the slurry to the pits, contaminated soil was mixed with cow manure, agricultural lime, starch or nutrisoy flour and phosphate buffers consisting of disodium phosphate and monosodium phosphate (54). The lined pits were covered with PVC caps, which were equipped with vents to allow the escape of gas emissions (54). Monitoring was done on a quarterly basis.

After a twelve month period the target toxaphene concentration of 25 ppm was achieved for 44 of the 45 treatment pits. The Old Red Lake Rd. treatment pit had a final concentration of 28 ppm (55). Project managers decided that there was no potential for human or livestock harm from

contamination at The Old Red Lake Rd. treatment pit and bioremediation was allowed to continue (55). The remaining 44 pits were uncovered, the PVC lining of the pit was perforated and the soil was allowed to dry. This process was followed by revegetation of the pits (55).

The total cost of this cleanup was more than originally anticipated. The volume of contaminated soil was found to be three to four times greater than previously estimated. Thus, it was necessary to request additional funds. The final cost of the project was over $4.5 million (56). This technology has the potential to be successful in cleaning up other sites where soil has been contaminated with other chlorinated compounds.

Land Application Case Studies - Andrews Environmental Engineering, Inc.

In 1994 Springfield, Illinois based Andrews Environmental Engineering, Inc. (AEEI) published a report for the Illinois Department of Energy and Natural Resources, which gave an overview of the land farming process and included eighteen brief case studies (57). The report was limited to small-scale pesticide waste generators. AEEI performed environmental audits at each of these sites and assisted in the submission of the land farming permit to the Illinois Department of Agriculture. Not all of the case studies presented cost analysis and no remediation results were presented in the report. The discussion here will be limited to the specifics of the audit and cost data for two case studies and general observations regarding the land farming cost summary by AEEI.

Alachlor Contamination. AEEI conducted an environmental audit of an unidentified site contaminated with alachlor. Samples collected around the loading pad, the former loading area, the liquid fertilizer tanks and the surface runoff area showed that Alachlor was present in the top six inches of soil at up to 210ppm (57). From these results AEEI decided to excavate and treat 603 tons of contaminated soil and 160 tons of contaminated gravel (57). For the land spreading operation 10.5 acres of field were required and the contaminated soil and gravel were applied by a truck-mounted soil spreader at a rate of 45 to 60 tons per acre (57). Corn was later planted on the same field. The total cost of this process was approximately $23,000, which is equivalent to approximately $30 per ton (57).

Railroad Site Contamination. A railroad company discovered pesticide contamination at a site that it had leased to a agrochemical company. The railroad company requested that AEEI audit the property. The audit revealed that the soil contained up to 2.6 ppm of Atrazine and up to 3.1 ppm trifluralin in the top six inches of soil (57). The total estimated volume of soil to excavated and treated was 9,718 tons (57). As of the printing of the report, 2,895 tons of contaminated soil and 625 tons of contaminated gravel had been excavated (57). Because of the volume of soil to be treated, the project was divided into two phases to be completed over the course of two years. Atrazine was applied at the rate of 60 tons per acre over 40 acres of land where corn would be later grown (57). Trifluralin was applied at the rate of 60 tons per acre over 123 acres of land on which soybeans would be grown (57). Based upon the volume of soil and gravel excavated at the time of printing, the cost of this project was approximately $76,000, which is equivalent to approximately $22 per ton (57).

Of the eighteen case studies presented by AEEI cost was addressed and explained for six. The average total cost for land farming at these six sites was $100,445 or $23 per ton (57). The two largest cost factors were engineering and spreading (21% each), followed by backfill (19%) and hauling (12%) (57). The remaining 27% of the total cost was composed of seven different factors, such as labor, excavation and testing (57).

Phytoremediation

Phytoremediation technology is still in the research and development stage and has not been widely implemented to cleanup pesticide-contaminated sites. The phytoremediation case studies that do exist generally involve the use of phytoremediation for heavy metal contaminated sites. There are no true case studies involving the phytoremediation of pesticides that present cost and performance data. Therefore, this discussion will be limited to a site where phytoremediation is being tested as an alternative to pumping and treating groundwater contaminated by pesticides.

Aberdeen Pesticide Dumps Site

Although there has been no final agreement on the clean up decision for the contamination at the Aberdeen Pesticide Dumps Site to date, the innovative use of phytoremediation thus far appears promising. The Aberdeen Pesticide Dumps in North Carolina is a former pesticide formulation plant. On site are four areas which were used for the disposal of the waste generated by pesticide formulation (58). At least seven responsible parties were identified by the EPA and they have been involved in the clean up effort (58). Several more parties have been identified and their participation in the clean up efforts is pending. Prior to treatment benzene hexachloride isomers, toxaphene, DDT, DDE, dibromochloropropane, xylene, ethyl benzene and toluene were all identified as pollutants in the soil and groundwater at this site (58).

Remediation at this site began with the removal of approximately 87,000 tons of contaminated soil for thermal treatment (58). This treatment was concluded in 1998. Phytoremediation is not being used as a means of degrading the contaminants at this site, rather it is being used to pump the groundwater from saturated zone in hopes of removing groundwater that could be potentially contaminated with residual chemicals (59). By using poplars to pump potentially contaminated water, it will lower the cost to use the pump and treat method to remediate the heavily contaminated groundwater. Any phytodegradation or rhizosphere enhanced biodegradation that occurs during this process is a positive side effect of the process, but not the intended goal of the responsible parties (59). A pilot-scale study was conducted in the spring of 1997 as a means of determining which plants to use and how the planting should be arranged (59). In the spring of 1998 the full-scale phytoremediation project began. The species chosen for phytoremediation at this site was the hybrid poplar (60). The depth of the planting ranged from 1.5ft to 12ft (59). By planting the trees so that their roots reached the capillary fringe, allowed the plants to rely exclusively on groundwater as their water source and draw up the contaminated groundwater (59). The surface vegetation intercepts and uses most of the precipitation, which contributes to the poplars dependance on the groundwater. The full-scale planting covers approximately 7.5 acres and consists of approximately 3500 trees (59, 60).

Currently, the plot is being maintained and wells are monitoring the groundwater movement. During the 1999 growing season approximately 4 million gallons of water were evapotranspired from the 7.5 acres based upon sap flow measurements (59). These results are promising. If the full-scale phytoremediation project in progress right now remains successful, it may replace all or part of the pump and treat activity (59). The final cleanup decision should be made within the next year (59).

Appendix B: Annotated Bibliography

The intent of this section is to provide a review of recent literature regarding bioremediation and phytoremediation. It is meant to give the reader an idea of the current state of the technology and to supplement Appendix C. No literature published prior to 1994 was considered in this section in order to provide only recent developments.

General Bioremediation and Phytoremediation References

The majority of these references are articles from scientific journals, however one presents information from the Air and Waste Management Conference, and another is an guide published by the U.S. EPA.

Anderson, J.A., Kruger, E.L., and J.R. Coats. 1994. Enhanced Degradation of a Mixture of Three Herbicides in the Rhizosphere of a Herbicide-Tolerant Plant. Chemosphere **28**: 1551-1557.

Interactions in the soil rhizosphere between plants and microorganisms have the potential to greatly enhance the rate at which soil contaminants are broken down. However, sites contaminated with herbicides present a unique problem because of their strong inhibition to plant growth. The authors of this paper aimed to test the ability of an herbicide-tolerant species to enhance rhizosphere degradation.

The study site was an agrochemical dealership in Iowa, which was contaminated with atrazine, metolachlor, alachlor and trifluralin. Three herbicide-tolerant plants were discovered on site: *Kochia* sp., knotweed (*Oiktgibyn* sp.) and crabgrass (*Digitaria* sp.). Soil samples were collected from the rhizosphere and from unvegetated areas. The rate of degradation for atrazine, metolachlor and trifluralin was tested by artificially contaminating the collected rhizosphere soil and incubating the samples for 14 days. Microbial abundance was estimated before and after treatment using the spread plate technique. The soil was analyzed for percent organic matter, pH, cation exchange capacity, and particle size distribution. Percent degradation was analyzed by extracting the remaining contaminants from the soil following treatment and quantifying them on a gas chromatograph.

Microbial numbers in the rhizosphere soil were one order of magnitude greater than the unvegetated soil. Unfortunately, the method that was chosen to quantify the number bacteria present was fairly selective and most likely underestimated the bacterial population by at least one order of magnitude. The degradation tests showed that the rhizosphere soil had a significantly higher rate of herbicide degradation when compared to the control soil. The results of this study show the importance of the rhizosphere microbial communities for the breakdown of organic contaminants. The authors suggest that it is the composition of the microbial community in the rhizosphere, rather than the size of the community that is important for herbicide degradation.

DeSchrijver, A., and R. DeMot. 1999. Degradation of Pesticides by Actinomycetes. Critical Reviews in Microbiology. **25**: 85-119.

The authors of this paper present a technical review of current information regarding the ability of certain species of actinomycetes to degrade the pesticides. Actinomycetes are filamentous bacterial species that are commonly found in the soil. The discussion is broken down by pesticide type. Organochloride pesticides, including a number of POPs chemicals are discussed along with organophosphates, triazines and several other types of pesticides. The authors discuss which species are capable of degrading which pesticides, along with the molecular mechanisms by which the bacteria breakdown the compound. This is a technical review, which only focuses on the microbial breakdown of pesticides and it does not approach any aspects of the remediation process.

Mulbry, W., Ahrens, E. and J. Karns. 1998. Use of a Field-Scale Biofilter for the Degradation of the Organophosphate Insecticide Coumaphos in Cattle Dip Wastes. Pesticide Science **52**: 268-274.

Along the US-Mexican border a series of dipping vats are used to control ticks that come into the US on Mexican livestock. The insecticide that is used in these vats is an organophosphate called coumaphos. Each vat contains approximately 1500 liters of solution at a concentration of about 1600mg/L. The recharging of all these dip vats results in approximately 460,000 liters of waste. At the time of the article's publication the spent dip vat waste was disposed of routinely in evaporation pits, which resulted in contaminated soil. The goal of this study was to test the efficiency of a field-scale gravel biofilter to degrade coumaphos, to test the effect of vitamin supplements on the rate and efficiency of degradation and to measure the rate at which residual coumaphos is mineralized in the soil.

Liquid coumaphos dip waste was transported from an operating dip vat site to the laboratory. The biofilter was built by modifying an agricultural storage tank. Fourteen layers of polyethylene foam pad were placed on top of a open grate and served as the filter, which was allowed to be colonized by microorganisms. The waste stream was recirculated at a rate of 229 liters per minute. The pH was maintained between 7.5 and 8 throughout the treatment. Following biofilter treatment some of the treated waste was incubated in flasks containing uncontaminated soil in an attempt to stimulate further degradation. This incubation was conducted for 110 days at 28 to 30°C on a rotary shaker.

Three trials were conducted with the biofilter system. In the first two trials a 200-fold reduction of coumaphos was noticed within the first 15 days. During the third trial, the biofilter became fouled and required cleaning. Following the cleaning, a sharp rise in the coumaphos concentration was observed. The fouling of the biofilter was attributed to the third trial and the concentration of coumaphos decreased when the filter rinsate was treated. Compared to previous laboratory tests using a smaller scale gravel biofilter, the polyethylene filter system was not as efficient. However, the polyethylene system was easier to maintain and less expensive. Because coumaphos is a chlorinated pesticide, the authors found that it was possible to monitor the remediation effort by the increase in chloride concentrations as the microorganisms dechlorinated the pesticide. Slight increases in coumaphos degradation were noticed when vitamins were added

to the biofilter. The soil incubation with biofilter-treated coumaphos waste indicated that approximately half of the residual coumaphos was capable of being degraded in this manner.

Based on the results of this demonstration, the USDA/APHIS program has selected this method for the treatment of coumaphos dip waste.

Mulbry, W.W., Del Valle, P.L., and J.S. Karns. 1996. Biodegradation of the Organophosphate insecticide Coumaphos in Highly Contaminated Soils and In Liquid Wastes. Pesticide Science **48**: 149-155.

This article also addresses the coumaphos waste that is produced at dip vat sites along the US/Mexican border for the control of disease-bearing ticks. The goal of these authors was to design and implement a biofilter system for the treatment of liquid coumaphos waste and to determine the success of treating coumaphos contaminated soil using bioremediation.

Soil samples were collected from eight dip vats sites. A phosphate buffer was added to the soil samples and they were incubated on a rotary shaker at 28°C. Some samples were augmented with cultured, coumaphos acclimated microorganisms and other samples were inoculated with elevated concentrations of coumaphos. For the biofilter experiment 30cm long columns were packed with either sand, pea gravel or diatomaceous earth. The coumaphos solutions were circulated through the filters at a rate of approximately 2 liters per minute.

Soil slurries from six of the eight sites resulted in rapid coumaphos degradation within seven days. The remaining two sites saw significant coumaphos degradation after a 40 day lag period. The addition of active coumaphos degrading microorganisms did not significantly enhance the rate of degradation. It was also observed that higher initial coumaphos concentrations generally led to a more rapid degradation. The biofilter system was capable of removing coumaphos from dip vat waste in seven to ten days at 25°C. Both the soil slurries and the biofilter resulted in complete metabolism of coumaphos and no intermediates were detected.

Mullins, D.E., Gabbert, S.E., Leland, J.E., Young, R.W., Hetzel, G.H. and D.F. Berry. 1998. Organic sorption/biodegradation of pesticides. Reviews in Toxicology **2**:195-201.

This article reviews the past projects which pertain to the removal and degradation of pesticides. The authors discuss the problems that have resulted from pesticide use and discuss the role of the US EPA and the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) in the regulation of pesticides. The goal of these researchers was to test the use of organic sorbents, which would sorb hazardous materials, such as pesticides, and facilitate their degradation by chemical and microbial methods. Such a system could be used as a pesticide disposal system.

Initial studies by these researchers showed that laboratory and field composting techniques were suitable for the degradation of pesticides, specifically diazinon. Peat moss, pine bark, steam-exploded wood fibers and various lignocellulose materials were all tested for their ability to act as pesticide absorbents. Based on the success of peat moss as a primary sorbent, a series of field tests were conducted. These tests resulted in the successful removal and degradation of various pesticides from pesticide rinsewater. The final study discussed the remediation soil contaminated

with either metolachlor or diazinon using a bioreactor that had been amended with vegetable oil and organic sorbents. The project had not been completed at the time of publication, but a reduced leachability of contaminants had been observed by the authors.

Prigge, C.E., Diener, R.G., Gartin, S.A., Lawrence, L.D., Hudson, D., and H.W. Hogmire. 2000. Benchtop Composting Reactor for Remediation Studies. Soil Sediment and Groundwater **June/July**: 16-20.

The intent of this research was to test a low cost benchtop composting reactor that would be used for feasibility investigations prior to choosing a remediation strategy for a site. This system was designed to duplicate the performance of the larger scale model that would be used for the actual site remediation.

The reactor core was constructed using polyurethane coated plywood. A plenum board with holes drilled through it was placed 5 inches from the bottom and provided uniform airflow through the reactor. Insulation was glued to the exterior of the reactor. A second plenum board, also with holes, was placed 5 inches below the bioreactor cover. A water trap was designed to condense and trap the gases produced by the reactor. A biofilter was attached to the opposite end of the water trap in order to treat odors and pesticide residues. A plenum board was also used in the biofilter to allow uniform airflow. Foam insulation was glued to the exterior of the biofilter. Newsprint and poultry manure were mixed to achieve the desired carbon to nitrogen ratio. The composting mixture was further adjusted by adding peat moss and water. According to the authors the bioreactor media was composed of equal quantities of finished compost mixture and woodchips. The reactor operated at an average temperature of 128°C for 16 days.

Over the course of treatment methyl parathion was reduced by 68%. The methods by which this was determined are not mentioned, nor are the degradation products. The article is also unclear as to which fraction of the composting media contains the original contaminated soil.

Showers, D.R., Norris, R.D., and A.N. Clarke. 1996. Treatability Studies for Pesticides Contaminated Soil from a Superfund Site: A Case Study of Six Technologies. Air & Waste Management Association, 89th Annual Meeting & Exhibition.

This report discusses the results of a feasibility study that was done as part of the Remedial Investigation at a pesticide-contaminated Superfund site in Florida. The technologies that were tested and compared were low temperature thermal desorption, two solvent extraction technologies, base-catalyzed decomposition and two bioremediation technologies. Several pesticides were identified at this site, including DDT, DDD, DDE and toxaphene.

Prior to the pilot-scale study discussed here, bench-scale treatability studies were conducted to determine if the technologies were suitable for the pilot-scale study. All of the pilot-scale studies were conducted by individual contractors. Soil was excavated from the site, screened and sent to the contractor for treatment. According to the authors, each contractor presented a protocol for their technology for evaluation by the consultant, the client and the U.S. EPA. The specific protocols are not discussed in this article, however a general overview is given for the application of each technology.

Thermal desorption treatment removed greater than 99% of the total pesticides present in the soil. The average retention time was 85 minutes and the cost was estimated between $155/ton and $205/ton. The triethylamine solvent extraction system removed greater than 94% of the total pesticides and the cost was estimated between $180/ton and $225/ton. Triethylamine is biodegradable, therefore the treated soil was allowed to be returned to the site as backfill. The critical fluid solvent extraction system demonstrated a removal efficiency range of 0% to 97% for individual pesticides. The average removal efficiency for the total pesticides ranged from 34% to 74%. The cost for this process was estimated between $125/ton and $150/ton. Base catalyzed decomposition resulted in 99% removal of total pesticides. The cost for this process was approximately $245/ton. Bioremediation using White-rot fungus was not successful, despite extensive fungal growth. DDD showed very little degradation, but no other pesticides showed any decrease in concentration. The treatability study, which was conducted prior to this pilot-scale study, showed a decrease in DDT, DDE and toxaphene concentrations. Due to its lack of success, no cost data was presented. Bioremediation using an aerobic/anaerobic cycle system degraded DDT by 65 to 91% and toxaphene by 76%. From this study it was estimated that for full remediation to pesticide concentrations below cleanup goals would, require four months. Costs for this process were estimated at $80/ton for *in situ* treatment and $120/ton for *ex situ* treatment.

Selection of the treatment technology for the remediation of the remainder of this site will depend on the final cleanup goals. Two technologies were carried forward to detailed evaluation. Low temperature thermal desorption has high potential for the treatment of excavated soil and aerobic/anaerobic cycling has the potential to meet cleanup goals in an *in situ* manner.

Singhvi, R., Koustas, R.N., and M. Mohn. 1994. Contaminants and Remediation Options at Pesticide Sites. EPA/600/R-94/202. US EPA. Office of Research and Development, Risk Reduction Engineering Laboratory. Cincinnati, OH.

This is an EPA document that was published in 1994 by the Risk Reduction Engineering Laboratory to aid in the decision making process for remedial managers. The introduction section briefly presents the problems that have resulted from pesticide use, and the policy issues that surround it. The second section discusses the historic use of pesticides, sources of pesticide contamination, and the different groups of pesticides and their chemical properties. This section also discusses such topics as compound behavior, fate and transport. The third section discusses the various technologies available for the remediation of pesticide-contaminated sites. The remedial options include containment technologies, stabilization/solidification technologies, vitrification technologies, thermal destruction technologies, chemical destruction technologies, biological destruction technologies, *in situ* and *ex situ* separation/concentration technologies and methods for the treatment of contaminated groundwater. The bioremediation discussion is useful, but lacks information on the important technological advances since the documents publication in 1994. The appendix to this EPA report includes a useful table that lists many of the National Priority List sites that are contaminated by pesticides, along with the method that has been chosen for remediation. No discussion of phytoremediation is included.

Zodrow, J. 1999. Recent Applications of Phytoremediation Technologies. Remediation. 9:29-36.

This publication is a review article that discusses different types of phytoremediation along with several recent applications of this technology. The discussion of the different types of phytoremediation explains the principles of the technique, along with its remediation potentials and limitations. After the broad scope of the introductory section, the author leads into some specifics regarding the state of the technology. Phytoremediation is an innovative technology that has been involved in several EPA SITE studies. Numerous studies have been conducted to identify hyperaccumulator plants and determine the feasability of using poplars and other trees that use large quantities of groundwater, for groundwater cleanup. Sewage and wastewater treatment using phytoremediation have also shown promise. The author mentions many individual remedial field studies at contaminated sites, but does not go into great detail. The author concludes by discussing cost considerations and recent developments. A lengthy discussion is not given to the applicability of phytoremediation to pesticide sites. This article is a good general overview of the current state of phytoremediation.

Battelle Conference Proceedings

Battelle sponsors three environmental remediation conferences: the International Symposium on *In Situ* and On-Site Bioremediation, the International Conference on Remediation of Chlorinated and Recalcitrant Compounds, and the International Conference on Wetlands and Remediation. The Bioremediation Symposium occurs on odd numbered years, while the International Conference on Remediation of Chlorinated and Recalcitrant Compounds occurs on even numbered years. Only one International Conference on Wetlands and Remediation has been held thus far and that was in 1999. The proceedings from these conferences are published in multi-volume sets grouped by subject matter. These articles provide valuable information regarding the most current state of the bioremediation and phytoremediation technologies.

Allen H.L., Mandel, R.M., Torres, M., Crouse, D.G., and T.F. Miller. 1999. Anaerobic Bioremediation of Toxaphene-Contaminated Soil. Phytoremediation and Innovative Strategies for Specialized Remedial Applications. A. Leeson and B.C. Alleman, Eds. Columbus, OH: Battelle Press.

The report by this group of researchers presents the data from a series of projects aimed at using anaerobic bioreactors for the treatment of toxaphene contaminated sites. Two of the studies were conducted at dip vat sites, where toxaphene had been used as an insecticide to treat livestock for parasites. One of the dip vat sites discussed in this article is the Navajo Dip Vats site which is also discussed in the Bioremediation Case Studies section of this report. The third test site was an aviation field that had been used for the aerial application of toxaphene to crops.

At each of the sites, pits were constructed and lined with plastic liners. Blood meal, limestone, water and phosphate buffer were mixed with the contaminated soil and poured into the pits. At the Navajo Vats site, sheep manure was also added to the contaminated soil as a bulking agent. The Navajo Vats site consisted of several study plots, whereas the aviation site had two treatment plots and the other dip vat site had only one treatment plot. The length of the individual studies varied from 40 days to 21 months.

Results at the Navajo Vats site showed toxaphene reduction from 58% to 86% for the five test sites reported. The time required for this reduction varied from 76 to 345 days. At the other dip vat site a 71% reduction was seen over a 14 day period. At the aviation site toxaphene was decreased by 95% and 94% in the two treatment plots over the course of seven months. The data presented here shows promise for use in future remediation projects. Currently, this technology is being implemented at the Navajo Vats Superfund site in order to remediate the many remaining vat sites.

Dott, W., Steiof, M., and B. Zettler. 1998. Biological Degradation of Chlorinated Aromatics in a Pilot-Scale Water Treatment Plant. Bioremediation and Phytoremediation: Chlorinated and Recalcitrant Compounds. Wickramanayake, G.B. and R.E. Hinchee, Eds. Columbus, OH: Battelle Press.

These authors conducted a pilot-scale *in situ* test to determine the feasability of purifying groundwater that had been contaminated by a pesticide production facility. Chlorobenzenes were the dominant contaminant at this site.

Laboratory tests have confirmed that microorganisms are capable of degrading chlorobenzenes, but few studies have been conducted demonstrating their ability to remediate these contaminants. The contaminated groundwater at the test site was located below a thick clay layer and was removed by six extraction wells. The groundwater was pumped into the treatment plant, which oxygenated the water, removed the iron hydroxide and then pumped the water into fixed bed reactors where microbial degradation occurred. Following microbial treatment, the water was passed through activated carbon filters, amended with nutrients and injected back into the groundwater aquifer.

The various different chlorobenzenes present in the groundwater degraded at different rates depending on the number and position of the chlorine substituents. Chlorobenzoles had a 95% degradation efficiency, the chlorophenoles had a 98% degradation efficiency and the hexachlorocyclohexanes had a 90% remediation efficiency.

Kim, I.S., Ishii, H., Sayles, G.D., Kupferle, M.K., and T.L. Huang. 1998. Biotransformation of Hexachlorobenzene by Anaerobic Enriched Cultures. Bioremediation and Phytoremediation: Chlorinated and Recalcitrant Compounds. Wickramanayake, G.B. and R.E. Hinchee, Eds. Columbus, OH: Battelle Press.

The fungicide hexachlorobenzene is toxic to most microbial species and it is known to persist in soils for decades due to its very low solubility. The goal of the research presented by these authors was to maximize the rate of anaerobic biodegradation of hexachlorobenzene by examining the potential of various microbial species supplemented with various cometabolites.

During the first study, anaerobic cultures were used to inoculate varying concentrations of hexachlorobenzene and subsampled every day for thirty days. The second study investigated the extent of hexachlorobenzene degradation over the course of 37 days by microbial cultures that had been obtained from three different sources. The first culture was acclimated to hexachlorobenzene, the second was acclimated to ethanol and the final culture came from anaerobic digester sludge at a wastewater treatment plant. Concentrations of hexachlorobenzene

and potential byproducts of its degradation were detected in the samples by extraction and analysis by gas chromatograph.

The results of the first portion of the study demonstrated that the rate of hexachlorobenzene degradation by hexachlorobenzene-acclimated microorganisms increased with increasing concentrations of the fungicide. Therefore, microorganisms that have been previously exposed to the fungicide are capable of degrading it quicker than those microorganisms that have not. They also respond in a dose dependent manner, degrading higher concentrations quicker than lower concentrations. At the highest concentration of hexachlorobenzene approximately 25 days were required to fully degrade it below detection levels. The second portion of the study showed that the hexachlorobenzene-acclimated culture was able to rapidly degrade the fungicide without a lag phase. The ethanol-acclimated culture was capable of degrading the fungicide, but it experienced a lag phase of approximately a week. The anaerobic digester sludge-acclimated microorganisms did not significantly degrade hexachlorobenzene. For all of the degradation processes, the major dechlorination product was 1,3,5-TCB.

Martin, M., Mengs, G., Martin-Montalvo, D., Sanchez, M., Garbi, C., Plaza, E., Ferrer, E., Fortun, A., Allende, J.L., Martinez-Inigo, M.J., and C. Lobo. 2000. Bioremediation of Soils and Waters Contaminated by Herbicides. Case Studies in the Remediation of Chlorinated and Recalcitrant Compounds. Wickramanayake, G.B, Gavaskar, A.R., Gibbs, J.T., and J.L. Means, Eds. Columbus, OH: Battelle Press.

Bioremediation can provide a low cost alternative to other remediation techniques. It also results in the complete destruction of the organic compounds, as oppose to other techniques, which may result only in the stabilization or disposal of the contaminant. The authors of this article believed that the use of microbial cells immobilized on a solid support would overcome some of the limitations of anaerobic bioremediation. Their goal was to test several bench-scale systems and a field system using immobilized cells for the removal of herbicides.

The microorganisms used in this experiment were grown in enrichment cultures containing either simazine or propachlor as the sole carbon source. Several experimental and one pilot-scale column were filled with various solid supports on which the bacteria were immobilized. Contaminated water was cycled through the columns at room temperature and at the rate of 50mL/min. A second bioreactor was designed to handle much larger volumes of wastewater. This trickling filter system could handle 220 liters at a time and used ceramic as the solid support for bacterial growth. A third system was demonstrated using contaminated soil inoculated with microbial cells which were suspended in a liquid media. The inoculated soil was incubated at 25°C at 65% relative humidity for 30 days under aerobic conditions. Samples were analyzed for residual herbicides using high pressure liquid chromatography and gas chromatography. Microbial growth and viability on the solid supports was monitored using confocal laser scanning microscopy.

Sepiolite and monolits were demonstrated to be the solid supports most beneficial to simazine remediation in columns. Sepiolite and alginate were shown to be the most beneficial solid supports for the remediation of propachlor in the columns. Remediation efficiency for the columns varied from 45% up to 86%. The pilot-scale bioreactor was successful at removing approximately 99% of the propachlor within 13 days. The large-scale bioreactor also efficiently

removed the herbicides present in the wastewater. All of the bioreactor systems showed significant microbial growth on the solid supports. Less than 20% of the propachlor remained in soil samples suspended in liquid media after 7 to 17 days of treatment using bioaugmentation.

Osano, A.A., Siboe, G.M., Ochanda, J.O. and J.O. Kokaro. 1999. Biodegradation of DDT: The Role of *Pleurotus* sp., A Lingnicolous Fungus. Bioremediation of Nitroaromatic and Haloaromatic Compounds. B.C. Alleman and A. Leeson, Eds. Columbus, OH: Battelle Press.

Many compounds that persist in the environment do so because they are unable to be degraded by the microorganisms that are present in the soil. Recent studies have overcome the persistence of DDT in soil through the innoculation of contaminated soil with white-rot fungi. The metabolic pathway by which white-rot fungi breakdown DDT and similar contaminants is different from the pathway which is used by bacteria. Most studies involving biodegradation by white-rot fungi focus on the species *Phanerochaete chrysosporium*. The research presented by these authors aimed to study the biodegradation of DDT by a different species, *Pleurotus luteoalbus*.

Growth medium containing DDT was inoculated with *Pleurotus luteoalbus* and incubated at 21°C for 30 days. Over the course of incubation the evolution of CO_2 was monitored. Following treatment, the media was analyzed for DDT using gas chromatography.

Over the course of the incubation three percent of the DDT was mineralized to CO_2. DDT was reduced by a total of 69% over the course of the treatment. Five byproducts of the DDT degradation were observed in the media, including DDD and DDE. Based on mycelial production, the authors concluded that the presence of DDT in the medium did not inhibit fungal growth. Although, only 3% of DDT was completely mineralized, the ability of this species of white-rot fungi to catalyze the initial step for the degradation of DDT is important for future research.

Torres, L.G., Santacruz, G., and E.R. Bandala. 1999. Biodegradatioin of 2,4-D and DDT at High Concentrations in Low-Cost Packaging Biofilters. Bioremediation of Nitroaromatic and Haloaromatic Compounds. B.C. Alleman and A. Leeson, Eds. Columbus, OH: Battelle Press.

The large volume of DDT and 2,4-D that have been used in Mexico has presented this country with the difficult problem of remediating many highly contaminated sites where these persistent pollutants exist. The goal of these authors was to demonstrate the ability of a biofilter with immobilized *Pseudomonas flourescens* to treat high concentrations of DDT and 2,4-D in water.

Samples from Mexico were not actually used in this project. Pesticide mixtures were prepared as stock solutions in methanol. Two test systems were designed. The first used a liquid bacterial culture, which was allowed to grow for 24hr prior to the addition of the pesticide solution. The second system used a glass column packed with tezontle, on which the pure strain of bacteria was immobilized. The pesticide solution was then passed through the column. Pesticide concentrations were monitored using gas chromatography, while bacterial growth was observed by optical density.

After 24 to 48 hours of treatment growth by *Pseudomonas flourescent* was generally equivalent to control samples, indicating that the pesticides did not inhibit bacteria growth. DDT removal efficiency varied form 58 to 99% in the treatment columns. 2,4-D was reduced by greater than 98%. Total organic carbon removal by the biofilter system ranged from 36 to 87%. From here the authors hope to optimize the system for use with actual environmental samples.

Van Leeuwen, J., Edgehill, R.U., and B., Jin. 1999. Biological Treatment of Wastewaters from Pesticide and Starch Manufacture. Bioreactor and *Ex situ* Biological Treatment Technologies. B.C. Alleman and A. Leeson, Eds. Columbus, OH: Battelle Press.

The goal of this project was to develop an effective treatment process for the remediation of industrial wastewaters. Two types of wastewaters were considered. The pesticide manufacture wastewaster had a high COD, and contained endosulphan 1 and 2, diazinon, malathion, atrazine, simazine and chlorpyrifos, among other pesticides. The remediation of starch wastewater that was presented by these authors will not be discussed in this review. The researchers tested the ability of ozonation, filtration, coagulation, activated carbon adsorption and biofilter treatment in order to remediate the pesticide manufacture wastewater.

The wastewater samples were obtained from a pesticide manufacturing facility. An ozone generator was used for the ozonation portion of the project. The biofilters were constructed by packing columns with gravel and allowing microorganisms from a sewage treatment facility to colonize them. 500mL batches of wastewaster were cycled through the biofilters over the course of a week at 100mL/hr. After four months, 2/3rds of the gravel was replaced with activated carbon. Ferrous sulfate was added to the biofilter-treated wastewater to coagulate suspended solids. The precipitate was then filtered and removed. The treated samples were analyzed for pesticides, total organic carbon, chemical oxygen demand, biological oxygen demand, total solids and total suspended solids.

The ozonation process removed the color, odor and 20% of the chemical oxygen demand. Biofilter treatment removed 88 to 95% of the chemical oxygen demand. Biological treatment was able to remove most of the pesticides from the wastewater with the exception of simazine. Activated carbon adsorption removed 80% of the chemical oxygen demand. Activated carbon was also sufficient for the removal of most pesticides with the exception of simazine. Microfiltration removed 86% of the chemical oxygen demand and 90% of the total organic carbon.

Williams, J., Miles, R., Fosbrook, C., Deardorff, T., Wallace, M., and B. West. 2000. Phytoremediation of Aldrin and Dieldrin: A Pilot-Scale Project. Case Studies in the Remediation of Chlorinated and Recalcitrant Compounds. Wickramanayake, G.B, Gavaskar, A.R., Gibbs, J.T., and J.L. Means, Eds. Columbus, OH: Battelle Press.

The goal of these researchers was to test the ability of several different plant species to enhance rhizosphere degradation of aldrin and dieldrin in addition to monitoring their ability to adsorb these pesticides.

The contaminated soil was collected from Fort Wainwright in Alaska. In addition to aldrin and dieldrin, the soil contained low concentrations of other organochloride pesticides. The experimental design used four different treatments using three types of plants. The north cell consisted of arctic hairgrass (*Deschampsia bernigensis*), the middle cell consisted of felt leaf will (*Salix alaxensis*), the south cell consisted of creeping red fescue (*Festuca rubra*), and the wet cell contained felt leaf willow and spikerush (*Eleocharis palustris*). The intent of the wet cell was to induce anaerobic dechlorination of the contaminants. The plants were selected based upon their predominance in the region. The cells were lined with a hydrophobic geotextile membrane, with the exception of the wet cell, which was lined with an impermeable liner to retain water. The cells were weeded, however the researchers were unable to prevent spikerush from overtaking the wet cell. It rapidly became the dominant species in the cell. Because of its dense root system, which may be beneficial for phytoremediation, spikerush was allowed to become part of the experiment. The plants were sampled at the end of each growing season.

The pesticide concentrations increased in the plant tissues each season. The latest sampling period showed that concentrations of aldrin and dieldrin in the plant roots was higher than the concentration of these pesticides in the soil. These results were unexpected due to the very strong sorption of these pesticides to soil particles. Although significant decreases in soil concentrations of these pesticides has not yet occurred, a significant increase in the pesticide concentrations in the plant tissues has been noticed. The explanation for this occurrence that these researchers are investigating involves the production of biosurfactants in the rhizosphere, which causes the pesticides to desorb from the soil.

U.S. Environmental Protection Agency Sponsored Web Sites

The websites and online databases presented in this section were of great importance in gathering information for this report. These sites were of particular value when I was searching for cost and performance data for the case studies.

clu-in.org - Hazardous Waste Clean-Up Information

This website is sponsored by the EPA's Technology Innovation Office and contains information on site remediation and characterization. The website is intended for use by citizens, students, teachers, engineers, researchers, remedial managers, vendors, and virtually anyone who has an interest. Electronic copies of many remediation and characterization reports (including this one) are available in the publications section of this website. There are links to other remediation and site characterization websites of interest. The Technology Innovation Office publishes a monthly newsletter called Tech Direct, which highlights recent publications and events of interest. Interested parties can sign up to receive the electronic newsletter at clu-in.org. Information on conferences and courses is also provided through this website.

www.epa.gov/ORD/SITE - Superfund Innovative Technology Program

The Superfund Innovative Technology Program (SITE) was established by the EPA's Office of Research and Development and the Office of Solid Waste and Emergency Response. The

program promotes innovative remediation, monitoring and measurement technologies at Superfund sites. The SITE program funds technology demonstrations that are proposed by the technology vendors. All demonstrations are pilot scale or full scale and are required to use an innovative technology that has some advantage over existing technologies. During the demonstration, the technology developer conducts the demonstration, while the EPA performs planning, sampling, QA/QC, report preparation and waste disposal. The reports that result from these demonstrations are available in .pdf format on the SITE website.

www.epareachit.org - Research and Characterization Innovative Technologies

EPA's REACH IT database is an extensive listing of various remediation and site characterization vendors, technologies and projects. Vendors voluntarily provide information on their technologies, services and on projects in which they have been involved. Because it is at the initiative of the vendor to provide and update the information in this database, some of it is incomplete and not up to date. Numerous technologies, vendors, and sites are represented in the database and it is a suitable starting point for gathering information for a report such as this. However, the information provided by the vendors should be verified before reporting. One particular vendor, who claimed to have extensive experience and information regarding the bioremediation of pesticides, appeared to have gone out of business. Some vendors list their technologies and sites multiple times in the database. Sites which are designated as EPA source sites generally had more reliable information. A search for full-scale bioremediation of organic pesticides and herbicides yielded 184 sites, of which eleven appeared in duplicate, six appeared in triplicate and one was listed in quadruplicate. This same search also yielded many unrelated sites. These results are presented in Figure C-1. Approximately two-thirds were not related to organic pesticides or herbicides.

www.frtr.gov - Federal Remediation Technologies Roundtable

The Federal Remediation Technologies Roundtable consists of the Department of Defense, the Department of Energy, the Environmental Protection Agency, the Department of the Interior, the Department of Commerce, the Department of Agriculture, The Tennessee Valley Authority, the Coast Guard and the National Aeronautics and Space Administration. The FRTR produces cost and performance case studies for remediation projects, which are update by the FRTR regularly. Currently, there are 218 studies listed in the database, including ten pesticide sites, three phytoremediation sites, and 33 bioremediation sites. The case studies presented in this database are extensive and provide useful

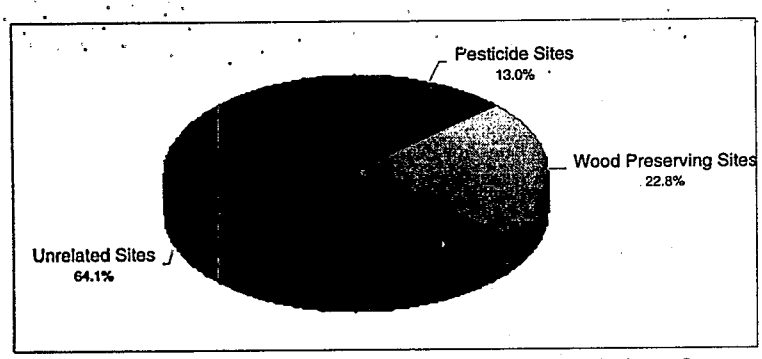

Figure C-1: Results of a query for full-scale bioremediation of organic pesticides/herbicides in the epareachit database.

information. The abstracts and case studies are published in hardcopy and the case studies are also available on CD-ROM.

In addition to the remediation case studies, the Federal Remediation Technologies Roundtable also publishes the Field Sampling and Analysis Technology Matrix and Reference Guide. The goal of this matrix is to provide a quick reference for screening, characterization and monitoring technologies. It provides information on technologies, their status, and the contaminants that they are capable of remediating. The quick reference is accompanied by a more extensive reference guide, which provides more information and bibliographic references.

Appendix C: Summary of Selected Bench Scale Experiments and Small Scale Field Experiments

Experimental Design	Contaminant(s)	Experiment Duration	Results/ Remediation Efficiency	Source
Bioremediation Studies				
White Rot Fungus biodegradation	DDT	30 days	69% of DDT degraded. 3% mineralized to CO_2.	37
White Rot Fungus biodegradation - several species of fungi	DDT	30 days	Species Dependent. Approx. 50% degradation. Approx. 5 to 14% of DDT mineralized to CO_2.	29
White Rot Fungus biodegradation - *Phanerochaete chrysosporium*	Mirex, aldrin, heptachlor, lindane, dieldrin, chlordane.	21 days	Chlordane: 9% to 15% metabolized to CO_2. Lindane: 23% metabolized to CO_2. No other compounds were significantly degraded.	10
Pesticide rinsewater absorbed by peat moss, followed by composting	Malathion, captan, lindane, diazinon.	Data Not Given	<2% of starting concentrations remained after treatment.	61
Biofilter used to remove contaminants from a liquid stream	2,4-D, DDT	168hrs	2,3-D: 99% removal. DDT: 58% to 99% removal.	62
Laboratory scale soil slurries and trickling biofilters for treating cattle dip vat wastes	coumaphos (an organophosphate)	7 to 10 days	Most soil slurries showed rapid mineralization. Biofilters decreased coumaphos conc. from ~1200mg/L to 0.02-0.1mg/L.	63
Field scale trickling biofilters for the treatment of cattle dip vat wastes followed by biodegradation in soil	coumaphos	30 days	Biofilter reduced conc. from 2000mg/L to 8-10 mg/L after 29 days. Vitamin supplements increased coumaphos degradation. Treated coumaphos degraded further in soil.	64
Biofilm and biofilm/activated carbon columns used to treat pesticide wastewater	Variety of pesticides, including organophosphates and triazines	greater than 4 months	Biofilm alone: 88% to 95% reduction. Biofilm/ Activated Carbon: >99% reduction and reduction in COD. Simazine was the only pesticide resistant to treatment.	21
Five different wastewater treatment processes	2,4-D, lindane, heptachlor	8 months	The facultative lagoon was the most effective process removing 73% of 2,4-D, 80% of Lindane and 62% of heptachlor.	11
Varioius oxic/anoxic cycling and oxic remediation methods using the DARAMEND™ technology	Isomers of hexachlorocyclohexane	405 days	Many different variations. Anaerobic/aerobic cycling was the most effictive process, however aerobic treatment did work. Range of remediation efficiency: 41-96%.	23

Appendix C (Continued)

Experimental Design	Contaminant(s)	Experiment Duration	Results/ Remediation Efficiency	Source
Contaminated groundwater bioremediation using a water treatment plant	Chlorobenzenes, chlorophenols, BTXE-aromatics and hexachlorocyclohexa nes	4 weeks	Degradation rate was highly specific to the position of chlorine substituents. Rapid dechlorination was noticed w/ monochlorobenzene, and ortho- and meta-substituted di- and trichlorobenzenes.	66
Anaerobic reductive dechlorination	Hexachlorobenzene	37 days	Complete degradation. Approx. 79% transformed to 1,3,5-trichlorobenzene	67
Combination of landfarming and biostimulation	Alachlor, metolachlor, trifluralin, and atrazine	60 days	80 to 85% alachlor reduction in contaminated soil. Complete reduction in alachlor-sprayed plots. Alachlor, metolachlor and trifluralin were all recovered least in cornmeal amended soil.	68
Anaerobic biodegradation field studies with nutrient supplements	Toxaphene	Several studies varying from 14 days to 21 months	Navajo Vats Site: 58% to 86% reduction after 3 to 12 months. Ojo Caliente Dip Vat Site: >70% reduction after 14 days. Sanders Aviation Site: 94% to 95% reduction after 7 months	69
Phytoremediation Studies				
Examined the use of the herbicide tolerant species, *Kochia*, to enhance rhizosphere degradation	Atrazine, metolachlor and trifluralin	14 days	Enhanced microbial degradation was observed in rhizosphere. 45% reduciton of atrazine. 50% reduction of metolachlor and 70% reduction of trifluralin.	70
Combination of composting and planting	Many present. Major pesticides: metoalchlor, pendimethalin, trifluralin.	40 days	50:50 mix of contaminated soil and compost maximized plant growth and minimized dilution. Rhizosphere had greatest bacterial activity w/contaminated soil/uncontaminated soil mix: Contaminated/Uncontaminated soil mix resulted in >95% metolachlor reduction	71
Phytoremediation using 3 different types of plant.	Organophosphates: malathion, demeton-s-methyl, ruelene.	8 days	Species Dependent. malathion: >83% reduction. demeton-s-methyl: >78% reduction. ruelene: no reduction up to 58%.	20
Phytoremediation using four different types of plant	Aldrin, Dieldrin	3 years	Species Dependent. Significant inc. in plant tissue concentration of both pesticides. Spikerush showed greatest inc.	23

Appendix D: Contact Information

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Appendix D (continued)

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