
The Use and Effectiveness of Phytoremediation to Treat Persistent Organic Pollutants

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This report is intended to provide an overview of phytoremediation uses to treat media contaminated by persistent organic pollutants and demonstrate the potential for use of phytoremediation in developing and transitional economies. It contains data compiled from a number of sources including literature and project documents, Internet sources, and personal communications. No attempts were made to independently confirm the resources used. The report is also available on the Internet at www.clu-in.org/studentpapers/.

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1. Introduction

1.1. Purpose

This project will investigate the usage of phytoremediation to treat soil and groundwater contaminated by persistent organic pollutants (POPs). The paper examines bench-, pilot-, and field-scale studies in which phytoremediation mechanisms have been applied. Data obtained from these studies will provide an overview of the effectiveness of phytoremediation work done to treat POPs. In addition, data will be used to demonstrate the potential of phytoremediation for use in countries heavily burdened by persistent contaminants.

1.2. Methodology

The chief sources of information on POPs for this report were Toxicological Profile Reports that were accessed from the Agency for Toxic Substances and Disease Registry (ATSDR) website. These Toxicological Profiles provided valid and comprehensive data on each of the POPs. Additional information on POPs came from a variety of sources, including the websites of organizations such as the World Wildlife Fund and the Pesticides Action Network, as well as the EPA's Office of Prevention, Pesticides, and Toxic Substances (OPPTS).

Data used to assess phytoremediation was extracted from a number of conference proceedings, EPA reports, technical documents, and background papers written on the technology. Primary sources of information on phytoremediation were the EPA's Technology Innovation Program website, the Hazardous Waste Clean-Up Information (CLU-IN) website, the Interstate Technology and Regulatory Council (ITRC), and data found in the *Remediation Technologies Screening Matrix and Reference Guide* on the Federal Remediation Technologies Roundtable (FRTR) website.

The focus of this report is the 12 POPs that the United Nations Environment Program (UNEP) classified as the most hazardous to human health and the environment (see Table 1).

Table 1. POPs Classified by UNEP

Pesticides		
Aldrin	Dieldrin	Mirex
Chlordane	Endrin	Toxaphene
Dichlorodiphenyltrichloroethane (DDT)	Heptachlor	Hexachlorobenzene (HCB)
Industrial Chemicals or By-Products		
Polychlorinated Biphenyls (PCBs)	Polychlorinated dibenzo-p-dioxins (dioxins)	Polychlorinated dibenzo-p-furans (furans)

The contaminants lindane, hexachlorohexane (HCH), atrazine, alachlor, and metolachlor, also are included in the paper, however, because they are persistent and share many of the same characteristics as the UNEP-classified POPs. Case studies were limited to laboratory (bench),

greenhouse (pilot), and field- and full-scale studies on POPs. Information on research projects included in the report were taken from conference proceedings, such as Battelle's International Conference on Remediation of Chlorinated and Recalcitrant Compounds, EPA Records of Decision (RODs), reports from database searches, and personal contacts. Data included is limited to the most recent data that was available. Citations for all references in this paper are included in Appendix 5.

2. Persistent Organic Pollutants

2.1. History and Development

Persistent organic pollutants were developed and used copiously without consideration of the possible detrimental effects. While many of these chemicals were developed in the early 1920s the agriculture and industry sectors of society became more dependent on them in the 1940s and 50s. Time, in conjunction with the progression of science and technology, has unveiled the damaging consequences of widespread and abundant usage. Awareness of adverse effects and regulation has increased in an effort to halt further destruction.

International attention was commanded by characteristics that make POPs a global threat: toxicity, persistence, bioaccumulation, and long-range transport. Over 120 different government and non-governmental organizations from across the world met in Sweden at the Stockholm Convention on Persistent Organic Pollutants in May 2001. In addition to establishing an international commitment to environmental protection, the convention called for the reduction and elimination of specified POPs. The convention resulted in the Stockholm Convention treaty, which became international law on May 17, 2004, for the countries that chose to ratify it. Since then, 90 parties have signed the treaty as well (see Appendix 1).

2.2. Description

2.2.1. Uses

Each POP shown in Table 1 above has multiple purposes that led to extensive use and subsequent environmental problems. Nine of the contaminants are pesticides, two are industrial chemicals, and two are unintentional chemical by-products. Pesticides, which make up the majority of the POPs, led to environmental hazards because of heavy agricultural use. Some developing countries still depend on these dangerous chemicals to fend off diseases. For example, DDT is used to kill vector-borne diseases like typhus and malaria. More detailed information on the specific uses of each contaminant is provided in Appendix 2.

2.2.2. Characteristics

The primary characteristics that all POPs share have led to increased regulation and global attention, which peaked at the Stockholm Convention. Toxicity, persistence, bioaccumulation, and long-range transport intertwine with and are affected by one another. Because a contaminant is persistent, it will last longer in the environment and, thus, has more opportunity to be transported on a global scale. This, in turn, spreads the chemical to new regions where more animals, in which it will bioaccumulate, can be exposed. These ripple effects can lead to extensive damage in the environment and health.

2.2.2.1. Exposure and Toxicity

Toxicity was a major criterion for including a contaminant in the Stockholm Convention treaty. Depending on dosage and route, exposure to contaminants can result in death. If exposure is not lethal, there are a number of other negative effects that these contaminants can have. Exposure route, toxicity, human health effects, and additional information are provided in Table 2.

Only primary and most frequent exposure routes for POPs are listed in Table 2. Toxicity data in Table 2 are based on male rats' acute oral exposure to the contaminant and are measured by the lethal dose at which 50 percent of the experiment population dies (LD₅₀), unless otherwise noted. Humans are more sensitive than animals thus, the animal testing presents relevant data. Lethality is contingent upon a variety of factors including the experimental population's sex, age, species, and diet. Listed health effects are those known to have direct effects to humans.

Table 2: Characteristics of POPs

Contaminant	Exposure Route	Toxicity	Health Effects	Comments
<i>Aldrin</i>	Ingestion of dairy products, fish, seafood, fatty meat, or root crops grown in contaminated soil or water	LD ₅₀ of 39 mg/kg	Fetus damage to pregnant women.	Aldrin is highly toxic to aquatic animals.
<i>Chlordane</i>	Ingestion of contaminated shellfish, meats, root crops, and other foods; maternal transference; occupational hazards; exposure to homes treated with chlordane; and exposure to waste sites contaminated with chlordane	LD ₅₀ of 83-590 mg/kg; estimated LD ₅₀ of 25-50 mg/kg of body weight in humans	Linked to liver, kidney, and blood disorders; damage to endocrine, cardiovascular, and reproductive systems.	Chlordane can be highly toxic to crustaceans, fish, and other aquatic animals.
<i>DDT</i>	Ingestion of contaminated foods; exposure to homes and other areas treated with DDT	LD ₅₀ of 113-800 mg/kg	Probable human carcinogen (USEPA). High levels may cause tremors and impact the kidney, liver, and immune and nervous systems. Low levels may cause nausea, diarrhea, eye, nose and throat irritation.	Correlation between DDT and mothers has been found in animals but still unknown for humans.

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<i>Dieldrin</i>	Ingestion of dairy products, fish, seafood, fatty meat, or root crops grown in contaminated soil or water	LD ₅₀ of 49 mg/kg	Fetus damage to pregnant women.	Dieldrin is highly toxic to aquatic animals.
<i>Endrin</i>	Ingestion of contaminated food, water, etc.	LD ₅₀ of 43.4 mg/kg	Carcinogenicity cannot be classified (USEPA); affects the central nervous system, liver; causes convulsions, etc.	Endrin can be highly toxic to crustaceans, fish, and other aquatic animals
<i>Heptachlor</i>	Ingestion of food contaminated with the substance; exposure to crops grown in contaminated soil; occupational hazards	LD ₅₀ of 40-162 mg/kg	Restricts reproductive abilities of men and women; has been detected in breast milk.	Heptachlor is a major component of chlordane; therefore, other effects may be similar.
<i>HCB</i>	Ingestion of contaminated foods; occupational hazards; close proximity to hazardous waste sites	LD ₅₀ of 19-245 mg/kg	Probable human carcinogen (USEPA). Chronic ingestion may result in liver, kidney, or thyroid cancer.	
<i>Mirex</i>	Contact with or ingestion of contaminated soil; inhalation and ingestion of contaminated food	LD ₅₀ of 740 mg/kg	Probable human carcinogen (USDHHS); increases risk of miscarriage.	
<i>Toxaphene</i>	Ingestion of contaminated shellfish, fish, water; close proximity to hazardous waste sites or stockpiles containing toxaphene	LD ₅₀ of 80-293 mg/kg	Probable human carcinogen (USEPA); damage to liver, lung, kidney, and nervous system; death from large doses.	

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<i>PCBs</i>	Contact with groundwater, soil, food, air, etc. contaminated by remaining PCB residues from industrial equipment, incinerated wastes, recycled oil, etc.	LD ₅₀ of 1010-4250 mg/kg/day	Probable human carcinogen (USEPA); acne, rashes, other skin conditions; irritated lungs and nose.
<i>Dioxins and Furans</i>	Ingestion of contaminated meats, dairy products, fish; occupational exposure; skin contact	LD ₅₀ of 22 µg/kg	Reasonably suspected to cause cancer (USDHHS); chloracne, red skin rashes; excessive body hair; changes in blood and urine that signal liver damage

Source: WWF 2005, Ritter et al. 1995, ASTDR a-j

2.2.2.2. Persistence and Bioaccumulation

Persistence refers to how long a substance stays in the environment, and bioaccumulation means that it is attracted to fatty tissue. Residues of most pollutants have been detected in air, soil, sediments, water, wildlife, aquatic animals, and other species all across the globe (WWF 2005). A contaminant can stay in the environment for a number of years before it downgrades into a less hazardous form. The concentration of the chemical will increase as it is consumed throughout the food chain. Thus, it bioaccumulates and becomes more dangerous (Stockholm Convention 2005). Bioaccumulation is extremely hazardous since pollutants are taken up by organic and other materials that are then consumed by small animals. As POPs accumulate in the fatty tissue of these small animals, each successive predator consumes a greater amount of the toxin. Often, this can be more fatal than one single dose (FAO 2005). These traits make the pollutants extremely dangerous and are the primary reasons that they are such a threat to health and the environment.

Because each contaminant is different, the levels of persistence and bioaccumulation may vary and may be affected by other factors. POPs do not dissolve well in water. While this means they are unlikely to contaminate groundwater, it also makes it difficult for the body to get rid of them. Aldrin, once in the body or environment, readily breaks down into Dieldrin; these two POPs will be discussed together. Dieldrin also fastens to soil particles, which makes it very resistant to leaching. Sunlight affects several of the contaminants, especially chlordane, slowing the breakdown process. Often, contaminants metabolites are more persistent than their parent products, as is the case with DDT and its breakdown products DDD and DDE. Areas of bioaccumulation are contaminant-specific as well. For example, DDT tends to bioaccumulate more in higher animals, while HCB is known to build up in grasses, wheat, certain vegetables,

and other plants. Endrin accumulates in small amounts in fatty tissues, and its residues normally cannot be found in the air. Persistence can be measured by half-lives—i.e., the amount of time it takes for a substance to degrade to half of its original amount. Depending on local climate and soil conditions, a contaminant can remain in the environment for days or decades (WWF 2005, Ritter et al. 1995).

Table 3: Contaminant Persistence in Soil

Contaminant	Persistence (in half-lives)
Aldrin/Dieldrin	5 years
Chlordane	1-3 years
DDT	2-15 years
Endrin	12-15 years
Heptachlor	Up to 2 years
HCB	2.7-22.9 years
Mirex	Up to 10 years
Toxaphene	100 days- 12 years
PCBs	.91-7.25 years
Dioxins/Furans	Over 20 years
Sources: WWF 2005, Ritter et al. 2005, ETOXNET 2001	

2.2.2.3. Mobility and Occurrence

Global transport of persistent organic pollutants has caused them to be distributed throughout the world, often in regions where they were never used, such as the Arctic. Low water solubility, semi-volatility, and high stability in the environment are characteristics that support long-range transport. POPs are ubiquitous in the environment, and they have been found in tropic regions, marine systems, and industrial areas (WWF 2005). Chemicals that are transported from warmer regions to more temperate zones degrade much slower because of the cooler temperatures (PAN 1998). Because they are more persistent in colder climates, contaminants permeate the environment and bioaccumulate easily. Once produced, chemicals can spread into sewers and streams, beginning a cycle that can eventually lead to circulation in the air and deposition as rain (FAO 2005). Contaminants used to treat homes for pests, such as chlordane, often are detected in the homes after treatment. Those that are produced by many different sources like PCBs, dioxins, and furans not only are found in all environmental media, but also can be found in the bodies of people (Stockholm Convention 2005).

Global transport is a direct connection to the occurrence of contaminants across the globe. Once distributed into various environments, contaminants can have unforeseen negative effects. A prime example of long-range transport can be seen in Midway Island, also known as Midway Atoll, a coral island found in the north Pacific Ocean between North America and Asia. The island is located 1,150 miles from Honolulu, 2,400 miles from Tokyo, and 3,100 miles from Los Angeles—i.e., far from any major industrial region. Despite this, DDT, PCB’s, dioxins, and furans have been found in black-footed albatrosses, local birds. Researchers discovered significant levels of the contaminants in the eggs, liver, fat, and plasma of the birds. Contamination led to eggshell thinning that caused deformed embryos and, ultimately, a drop in nest productivity. The DDT, PCBs, dioxins, and furans possibly were transported to the atoll by semi-burned plastics and municipal waste incineration operations from countries that border the

Pacific Ocean. Also, a plume of DDT on the coast of Southeast Asia may have been the cause of the population decline (FAO 2005, U.S. Water News Online 1996). Residues of aldrin/dieldrin and heptachlor also have been found in bird eggs and tissues, and have been linked to declining populations of wild birds. Cases of DDT similar to that in Midway Island were cited in U.S. bald eagle populations. DDT was found to reduce reproductive rates by causing the eggshells to thin, making them break easier, and ultimately resulting in the death of many embryos (WWF 2005).

POPs like pesticides often are overused or used improperly, and this has led to another concern. Many species build up a resistance to the active ingredients, rendering them ineffective. Also, damage often is done to the natural organisms that would regulate pest populations and to other non-target organisms. This causes a series of changes to the ecosystem and inhibits the function of soil microorganisms (FAO 2005, PAN 1998).

2.3. International Issues

For decades, abundant use of POPs across the globe has been a problem, and it has increased with time. The Food and Agriculture Organization (FAO), the Global Environment Facility (GEF), the UNEP, and other organizations recognize the urgency of the issue and are actively working to bring attention to it. Improper storage, disposal, and continued use of pesticides, the majority of POPs, in developing and transitional economies presents a massive threat. Pesticides have accumulated for many reasons, including:

- Out of season donations,
- Poorly timed donations,
- Aggressive marketing, distribution, and promotion of products,
- Inability to accurately time pest outbreaks,
- Inadequate containment and storage facilities,
- Inappropriate usage, and
- Mislabeling.

The contaminants cause major problems, because they often leak, are misused, and are located near homes. Since most of the containers are old and the pesticides are past their expiration dates, they generally drip with rust and aged toxins. Some leftover pesticides spill or are dumped into the streets and, consequently, pollute locally and beyond. Storage containers generally are old drums and lend themselves to convenient domestic uses such as plant potting, and food and water storage. Often, local residents bring the containers into their homes, unintentionally exposing themselves and their families to the dangers associated with the contaminants (FAO 2005).

Primarily located in African and Eastern countries, tons of old and unused pesticides are wreaking havoc across the globe, and there are undoubtedly more that have not been discovered yet. A list of countries in Africa and the Middle East where obsolete pesticides have been inventoried and amounts have been estimated is provided in Appendix 3. Contaminants are located in old warehouses, buried underground, or left in open dumps. These obsolete pesticides often are stored in bulk. These stockpiles plague a variety of countries such as, Rwanda, Nepal, and Poland (FAO 2005, Chaudhry et al 2002).

Twenty thousand tons of obsolete pesticides are located in Africa alone (see Figure 1), and this realization has brought attention to the previously neglected subject. Dieldrin once was used throughout Africa to control locust outbreaks. Most storehouses with dieldrin were never cleared after the pesticide was banned, leaving it to be used by local farmers in need or for other unregulated uses (FAO 2005).

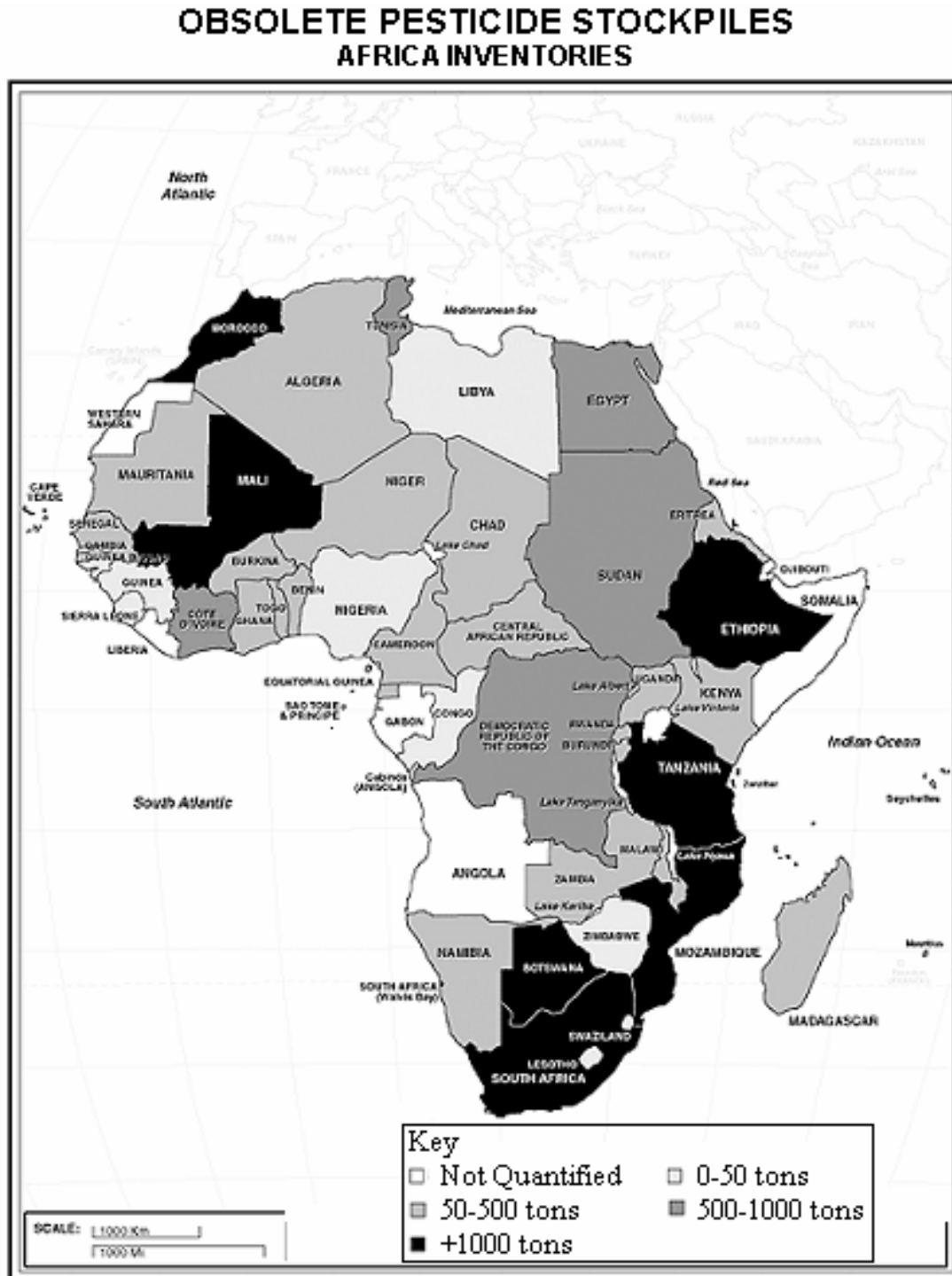
Rwanda is one of many countries plagued by POPs, and its efforts are indicative of a growing awareness of the contaminants' dangers (Karemera 2002). Rwanda is one of the least developed countries in the world by social, economic, and typical political standards. It is a country still recovering from devastating civil war, and its economy is highly dependent on basic farming and agriculture. Increasing levels of POPs have made the contaminants a major issue for the Rwandan government, as well as those of many other African countries. An inventory conducted in Rwanda indicated that the major sources of POPs include:

- Iron works,
- Wood and fuel combustion,
- Heavy oil electric transformers,
- Chemical hair treatment,
- Drycleaning, and
- Landfills stocked with obsolete pesticides.

Efforts to clean up POPs have taken place in other countries. During 2001 and 2002, a major effort to clear out the contaminated stockpiles of obsolete pesticides in Nepal was spearheaded by Greenpeace. Most of the pesticides were found to be in decomposing original packaging. Seven locations in Nepal were found to contain over 70 tons of obsolete pesticides, including dieldrin, DDT, and other contaminants. Local residents had complained of headaches and nausea. Most of the pesticides were manufactured years ago and were imported as donations from western countries' major chemical companies (Greenpeace 2002).

The country of Poland discovered large amounts of problem-causing pesticides deposited in tombs. Tombs are bunkers that have a concrete ring anywhere from one to three meters in height and are located underground with top and bottom concrete lids. These tombs have been around for over 30 years. The 350 tombs that were found contained a total of 10,000 tons of obsolete pesticides. Seventy-five percent of these pesticides consisted of aldrin, dieldrin, DDT, HCB, heptachlor, and toxaphene. There were approximately 400 tons of DDT, 190 tons of toxaphene, and similar levels of the other POPs, except for heptachlor of which less than one ton was found. The concrete walls of the tombs proved to be insufficient in containing the pesticides. Leaching, which pollutes groundwater, and flooding became a major concern because the pesticides were located underground (Czaplicki et al. 2002). The tombs represent only a fraction of the pesticides located in Poland. Thousands of other obsolete pesticides are stored improperly on local farms and in warehouses. About 120 tombs, or underground dumps, containing DDT and lindane have been found in Latvia and Bielarus, countries surrounding Poland (Chaudhry et al. 2002).

Figure 1



Source: www.africastockpiles.org

2.4. Alternatives and Limitation

No longer beneficial for their intended uses, obsolete pesticides contaminate water and soil, and PCBs, dioxins, and furans continue to be produced through chemical manufacturing. Alternatives often prove too costly and risky for utilization. Some alternatives also may be more complicated and, as a result, too difficult for developing economies to implement. Despite the Stockholm Convention, some countries support the continued use of certain POPs such as aldrin and dieldrin. Time, technology, and funding are the factors that influence countries to transition to safer alternatives (see Table 4) and clean up methods (Stockholm Convention 2005, WWF 2005)..

Table 4: Alternatives for POPs

Contaminant	Alternatives
<i>Aldrin/Dieldrin</i>	In cotton production aldrin/dieldrin can be replaced by Integrated Pest Management (IPM). ¹ To control termites, natural repellents may be used, as well as physical barriers, biological pathogens, and parasites. Climate and building and soil type are determining factors.
<i>Chlordane</i>	IPM may be used as well as Integrated Vector Control (IVC) ² technologies.
<i>DDT</i>	DDT is one of the more difficult pesticides to replace, because many countries are dependent on it for control of malaria. Alternative chemicals can be used to spray homes and treat bed nets. IVC can be promoted in the place of DDT use.
<i>Endrin</i>	IPM is one of many alternatives.
<i>Heptachlor</i>	IPM Native shrubs were found to be effective in Kenya to combat termites instead of heptachlor. Replace materials used to protect electric power transformers and underground television and cable boxes.
<i>HCB</i>	Prevention of pollution and use of clean production systems and materials are options. IPM Processes that use chlorinated solvents should transition to non-chlorinated solvents or alternative processes. For example, traditional drycleaning can be replaced with multi-process wet cleaning, which utilizes steam, heat, water, natural soaps, and vacuum to clean clothes.

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<i>Mirex</i>	IPM On leaf cutter ants, plastic skirts saturated with adhesives or sap can be used, along with other physical barriers. Wastes from other ant colonies also may be used, along with lemongrass or other effective alternative repellents. Once a building is invaded with termites, extreme heat or cold may be used to kill the termites.
<i>Toxaphene</i>	IPM
<i>PCBs</i>	Non-incineration destruction technologies Biodegradable substances like mineral and silicone oils
<i>Dioxins and Furans</i>	Because dioxins are emitted as a by-product of other processes, it is difficult to replace them; reduction is the best method to control them. Industrial process and other sectors can switch to chlorine-free chemicals. For example, chlorine-free plastics like polyethylene and materials like glass and steel can be used instead of PVC. Oxygen, ozone, and peroxide can be used instead of chlorine-containing products can be used to bleach paper. Non-combustion technologies and waste management systems that use separation and re-use methods should be used.

¹ Integrated Pest Management (IPM) is an innovative technology that uses a number of methods such as the re-introduction of useful insects, mechanical cultivation, crop rotation, and planting varieties of crops that mature prior to invasion by insects. The method can be very effective but is generally site-, crop-, and/or insect-specific (WWF 2005).

² Integrated Vector Management (IVM) is a three-part technology used to control vector-borne diseases. It includes: Attacking the pathogen using immunization or other drugs when possible; attacking the vector using biological or chemical methods; and reducing human contact with mosquitoes and increasing public education.

While the use of alternatives may be uncertain, environmental and human health hazards demand the cleanup of remnants from previous uses of POPs. In consideration of the cost-efficiency and widespread availability of plants, phytoremediation is a front-runner among technologies to clean up persistent organic pollutants.

3. Phytoremediation

Phytoremediation is an innovative and progressive technology that uses plants to rid soil, groundwater, air, sediments, and surface water of contaminants. Phytoremediation is comprised of several different techniques that utilize vegetation, its related enzymes, and other complex processes. Collectively, these processes are able to isolate, destroy, transport, and remove organic and inorganic pollutants from contaminated media.

3.1. History

While phytotechnologies have gained attention over the last several years, the processes have been taking place naturally for over three centuries. Throughout the 1970s and the following decades, plants were heavily tested and used to treat soil infiltrated with metals and contaminants in wetlands. As a result, techniques for these uses are well established (McCutcheon et al. 2003). Widespread use of phytoremediation by federal and state governments, as well as non-governmental organizations, began in the 1980s (EPA 2005b). The use of the term phytoremediation was initiated by the EPA in 1991, and it was first used in open technical

literature in 1993 by Cunningham and Berti. In the late 1990s new uses for phytoremediation were discovered, and it became known among innovative scientific technologies (McCutcheon et al. 2003). Phytoremediation was derived from other fields such as agronomy, forestry, chemical and agricultural engineering, microbiology, and many others. Since its inception it has developed into an independent field of study and a widely applicable technology (Tsao 2003). Bench-, pilot-, and field-scale research continues to provide information and insight for future exploration and application.

3.2. Uses

As phytoremediation gains popularity, there are constantly new ideas on how and where it can be applied. Phytoremediation has been applied at several sites on the National Priorities List, as well as other hazardous waste sites, to help meet regulatory requirements. The diversity of pollutants to which it can be applied—crude oil, metals, explosives, pesticides, chlorinated solvents and numerous other contaminants—is the prime reason the technology has developed rapidly (EPA 2005b). Phytoremediation has become not only an interest of universities and major research centers, but also has created a new business for contractors and consulting firms.

Phytoremediation consultants are able to advise stakeholders about whether phytoremediation would be the best cleanup method for their sites, and contractors are able to install the selected remediation system. The U.S. market for phytoremediation was estimated at between \$30 and \$49 million in 1999 and has since grown (Glass 1999, 2005). Phytoremediation is studied heavily in Canada and the United States and draws sincere interest abroad. Phytoremediation projects are underway in Ukraine, Sweden, Switzerland, Czech Republic, China, and Poland, to name a few.

3.3 Mechanisms

There are several mechanisms used to treat contaminated sites that take place outside, inside, or through plant systems. Rhizodegradation and phytodegradation are most effective with organic contaminants, while phytoextraction is best with inorganics. Some mechanisms, like phytovolatilization, are equally effective with inorganic and organic contaminants (Tsao et al 2003).

Phytoremediation mechanisms include but are not limited to:

Phytodegradation (PD)—Also known as phytotransformation. Contaminants are taken up by plants and then undergo breakdown by metabolic processes within the plant tissue.

Phytoextraction (PE)—The most commonly used mechanism; also known as phytoaccumulation. Contaminants are taken away from the media and accumulate in plant shoots and leaves.

Phytostabilization (PS)—Contaminants are disabled and prevented from migrating through accumulation and absorption.

Rhizodegradation (RD)—Plant roots enhance microbial activity in the root zone, and microorganisms breakdown contaminants.

Phytovolatilization (PV)—Contaminants are released into the atmosphere after uptake and transpiration.

Hydraulic Control (HC)—Contaminants are removed from groundwater through uptake and consumption, and their spread is contained and/or managed.

Use of a specific technique is dependent on site characteristics and contaminants being treated (EPA 2001, EPA 2000, Glass 2005).

3.4. Benefits and Limitations

Phytoremediation has numerous advantages that foster acceptance on a broad scale. Primary advantages are:

- As a solar-driven system, phytoremediation takes advantage of natural plant processes, and thus lowers labor, equipment, and operational expenses.
- Planted sites generally are more attractive than other choices.
- Lower air and water emissions and secondary waste production makes phytoremediation a safe treatment.
- Phytoremediation controls runoff and soil erosion.
- Phytoremediation can be used in conjunction with other remediation methods and, therefore, may be more beneficial than a stand-alone technology.

Other benefits of phytoremediation include: Control of fugitive dust emissions, reduced noise, fewer health risks for workers, increased biodiversity, and high public approval.

As researchers continue to expand and improve the applications of phytoremediation some limitations remain. Primary limitations are:

- Root Growth—Remediation is based on contaminant contact with plant roots and cleanup is only as deep as the roots reach.
- Lengthy Time for Remediation—The time for plant growth slows the process down.
- Phytotoxicity—Plants need to be tolerant of contaminants.

Additional disadvantages that should be noted are: Local climate conditions, planting space, seasonal nature of plants, and possible transmittance of contaminants to surrounding creatures.

All advantages and limitations may not be applicable to each mechanism of phytoremediation. Although phytoremediation has proven to be an effective and efficient method, it is a site-specific technology. Deeper root growth and higher contaminant tolerance are possible through the development of specially engineered plants. More information can be obtained from the Interstate Technology Regulatory Cooperation. (EPA 2001, EPA 2000, Glass 2005).

4. Research and Applications

4.1. History and Overview

Many studies have been conducted to examine phytoremediation mechanisms. Generally, studies have focused on identifying and learning which contaminants are most responsive to certain mechanisms. Phytoremediation of many contaminants, such as organics, has been researched

extensively; however, the use of phytoremediation to cleanup POPs is relatively new (Watanabe 1997).

In the early stages of phytoremediation, plants were reportedly not capable of degrading DDT. In 1977, however, scientists found that certain cell suspension cultures of *Petroselinium hortense* and *Glycine max* were able to degrade ^{14}C DDT (Suresh et al. 2005). Over the years phytoremediation of DDT was studied frequently. Cultures of aquatic plants were shown to degrade DDT to its metabolites in 2000. More information on the use of non-target plants and plant tolerance and sensitivity is provided by Karthikeyan et al (Karthikeyan et al. 2004). Studies continue to examine and present possible solutions for phytoremediation of DDT and other POPs.

Phytoremediation for other contaminants, such as PCBs, is even more recent. For years researchers thought that phytoremediation would not be successful with highly hydrophobic contaminants, like PCBs. PCBs were found in the bark of black walnut and tulip poplar trees in 1987, but specific mechanisms were not widely studied until years later (Meredith and Hites). More recent studies focused on phytoremediation of PCBs have shown that zucchini to be quite successful at extraction. Early field studies in 1994 also found congeners of dioxins and furans were found in the leaves and fruits of zucchini (Campanella et al. 2002). Atrazine has been extensively studied in recent years as well (Suresh et al. 2005). Contaminants such as endrin, toxaphene, heptachlor, and mirex have not been studied as widely.

Frontrunners in phytoremediation research, The Royal Military College of Canada and the Connecticut Agricultural Experiment Station, as well as other scientists have identified certain plants that are especially successful at phytoremediation through greenhouse and plot studies. Plants like pumpkin, sedge, tall fescue, and zucchini have been found to be the best at phytoextraction of PCBs. Pumpkin, zucchini, and squash also were found to be successful when used for phytoremediation of DDT, DDE, and DDD (Lunney et al. 2004, White 2002, White et al 2003, White and Mattina 2004, Zeeb et al 2004). In addition, a recent laboratory study showed that hairy root cultures (*Cichorium intybus*) are promising in the degradation of DDT (Suresh et al. 2005).

4.2. Case Studies

The majority of studies included in this report focus on PCBs, DDT and its metabolites, and atrazine. The primary mechanism used in these studies was phytoextraction (20 of 37 studies). Rhizodegradation was also used frequently (12 studies). The rest of the studies discuss a mix of mechanisms including hydraulic control, phytodegradation, and phytovolatilization, which was the least used. A variety of vegetation was used and included hybrid poplars, zucchini, pumpkin, grasses, etc. The studies were divided into three sections: bench, greenhouse and plot, and full-scale.

4.2.1. Bench Scale Studies

Bench-scale studies are defined as laboratory research. Six of the eight bench-scale studies were done through an academic institution. Laboratory research on atrazine dates back to 1996. Studies of PCBs are relatively new (2001), although one study was found on PCB-degrading

bacteria in 1994. Atrazine is the contaminant treated in three of the studies. Two studies focus on DDT and/or its metabolites, and there is one study each on HCB, PCBs, and chlorinated benzenes. The primary mechanism used was rhizodegradation; phytoextraction and phytovolatilization also were used. A variety of vegetation was used in each study and included poplar trees, burr medic, canary grass, etc. Results of bench-scale studies, along with the contaminant treated, concentration levels, media, vegetation, mechanisms, involved parties, and year of the study can be found in Appendix 4.

4.2.2. Greenhouse and Plot-Scale Studies

Greenhouse and plot-scale sites constitute the majority of studies (16 of 37) in this report and date from 1991 to 2005. Plot studies are generally small field studies; greenhouse and plot studies are used as test experiments, sometimes in preparation for a larger application. Eight of the studies treated DDT, DDE, or DDD, and five treated PCBs. Other contaminants examined were atrazine, HCH, alachlor, chlordane, and metolachlor. Phytoextraction was the mechanism used in 12 of the 16 studies. Two studies used rhizodegradation, one used phytodegradation, and one was unaccounted for. Vegetation used included zucchini, pumpkin, and different grasses. Refer to Appendix 4 for a table of greenhouse and plot studies that used phytoremediation to treat POPs. The table includes the site name or study title, contaminants treated, mechanisms used, involved parties, date, and other information where provided.

The Royal Military College of Canada in Kingston, Ontario has performed a three-part pilot-scale study to exam the uptake of PCBs by pumpkin, fescue, and sedge. The study began in 2004 and has progressed into a full-scale study. Details are given in the case study on the next page.

Greenhouse/Plot Case Study

Study: “In Situ Phytoextraction of PCBs from Soil: Pilot-Scale Field Trial”
Location: Etobicoke, Ontario

<i>Greenhouse Treatability Study- In situ</i>	<i>Small Field Experiment- Ex situ</i>	<i>Full-Scale Study</i>																								
<p>Traditionally, it has been thought that highly hydrophobic contaminants such as PCBs would not be taken up at any major levels. Based on large root systems, link to microbial activity, release of root exudates, and other factors, several species were tested for their uptake potential. Soil was taken from a site that was once an electrical transformer manufacturing facility. Aroclor 1260 (PCBs) contaminated the soil at concentration levels ranging from 27.5 to 3050 µg/g.</p> <p>Plant trays were covered with parafilm to minimize volatilization. This greenhouse experiment deemed the pumpkin (<i>Cucurbita pepo cv. Howden</i>) and tall fescue (<i>Festuca Arundinacea</i>) as the best species. Also, a third species which performed well in similar studies was selected for the following phase. Plant uptake is shown in the chart below.</p> <table border="1" style="margin-left: auto; margin-right: auto; border-collapse: collapse;"> <thead> <tr style="background-color: black; color: white;"> <th></th> <th>Roots</th> <th>Shoots</th> </tr> </thead> <tbody> <tr> <td>Pumpkin</td> <td>730</td> <td>16.8</td> </tr> <tr> <td>Fescue</td> <td>440</td> <td>6.2</td> </tr> <tr> <td>*Sedge</td> <td>1200+</td> <td>470</td> </tr> </tbody> </table> <p>Measured in µg/g; *Data from other studies</p>		Roots	Shoots	Pumpkin	730	16.8	Fescue	440	6.2	*Sedge	1200+	470	<p>The second experimental phase was performed as a small field test. This field study was performed using larger containers and no coverings. These changes allowed plants to grow faster and larger and did not limit plants’ access to volatilized PCBs.</p> <p>The three plants that were chosen from the previous study were planted in outdoor pots with soil from the site. PCB concentrations increased greatly in the roots and shoots of the plants as shown in the chart below.</p> <table border="1" style="margin-left: auto; margin-right: auto; border-collapse: collapse;"> <thead> <tr style="background-color: black; color: white;"> <th></th> <th>Roots</th> <th>Shoots</th> </tr> </thead> <tbody> <tr> <td>Pumpkin</td> <td>790</td> <td>370</td> </tr> <tr> <td>Fescue</td> <td>805</td> <td>580</td> </tr> <tr> <td>Sedge</td> <td>785</td> <td>410</td> </tr> </tbody> </table> <p>Plant uptake measured in µg/g.</p> <p>The results of this phase of the study demonstrated to researchers that no significant amounts of PCBs were released into the environment through volatilization. Water that passed through the soil also was tested and found to be PCB-free.</p>		Roots	Shoots	Pumpkin	790	370	Fescue	805	580	Sedge	785	410	<p>The initial stages of the experiment process led to a full-scale study at the actual Etobicoke site just outside of Toronto. The project was started in 2004 and is ongoing. Soil contamination at the site is relatively low-about 25 ppm. However, Aroclor 1254 and 1260, the PCB contaminant, is highly chlorinated and weathered. These factors contribute to an increased recalcitrance.</p> <p>To date, the plants at the site have not show high extraction levels. Concentration levels in the plants are still below that of the PCB concentration in the soil.</p>
	Roots	Shoots																								
Pumpkin	730	16.8																								
Fescue	440	6.2																								
*Sedge	1200+	470																								
	Roots	Shoots																								
Pumpkin	790	370																								
Fescue	805	580																								
Sedge	785	410																								

Sources: Whitfield 2005, Whitfield et al. 2005

4.2.3. Full-Scale Studies

Full-scale studies involve actual sites where contaminants have infiltrated the soil or groundwater, and phytoremediation has been applied. Thirteen full-scale studies are included in this report and date from 1987 to 2005. PCBs were the contaminants treated in five of the studies, atrazine in four, and alachlor in four. Six studies used rhizodegradation, and six used phytoextraction. Other mechanisms used were hydraulic control (4 studies), phytodegradation (2), phytostabilization (2) and phytovolatilization (1). Hybrid poplars and grasses were the main vegetation used. Refer to Appendix 4 for details, including the year, contaminant treated, media, vegetation, mechanism used, involved parties, and other data where provided.

Full-scale application of the technology has taken place at sites regulated by the EPA as well as at sites where parties voluntarily implemented remediation. Sites with federal oversight undergo a number of evaluations as well as regulatory monitoring. Because many of the full-scale applications of phytoremediation are not complete yet, it will be some time before their results are known.

In 1988, a full-scale treatment began at a site in Okonee, Illinois, to treat atrazine, alachlor, and metolachlor that contaminated soil and groundwater. Details of the site and the process of phytoremediation treatment are given in the case study on the next page.

Full-Scale Case Study

Site: Okonee, Illinois

Prior to 1988, farm chemicals were manufactured at this one- to three-acre-acre site for the retail farming market in Okonee. Chemicals produced were atrazine, alachlor, and metolachlor, along with other pesticides, nitrate, and ammonium. The groundwater, which reached depths of six to ten feet below the surface, and soil were highly contaminated. After evaluation of the silt-to-silty-clay soil and the groundwater at the site, phytoremediation was chosen as a remedy.

Phytoremediation was implemented at the site to clean the soil and to inhibit off-site migration of the contaminant plume. Initially, alfalfa and corn were used to reduce the high levels of pesticides. Within the first three years after phytoremediation was applied, the pesticide levels decreased significantly. Following this, grasses were planted to serve as a treating medium for a modified pump-and-treat system that was installed. The next phase of the phytoremediation began in 1992, when hybrid poplars were planted to serve as a source of groundwater extraction and to limit contaminant migration. The trees grew consistently at a range of six to eight feet each year. The contaminants in the soil and groundwater responded by continuously decreasing (see results below).

The site was maintained with pruning, mowing, and drip irrigation. Weather and soil moisture conditions, and groundwater elevations at the site were monitored.

Approximate Levels of Contamination in Groundwater

Year	Atrazine	Alachlor	Metolachlor
1988	1,600	1,980	1,850
1996	75	170	380

Measured in parts per billion (ppb)

Approximate Levels of Contamination in Soil

Year	Atrazine	Alachlor	Metolachlor
1987	885	180	80
1990	10	25	25

Measured in parts per million (ppm)

Sources: Phytoremediation 2000e, TreeMediation 1999

4.3. Promising Techniques

The use of certain mechanisms, plants, or enhancements can enhance the effectiveness of phytoremediation on persistent organic pollutants. One of many promising techniques is an integrated multi-process phytoremediation system (MPPS). MPPS is composed of three parts: volatilization, photo-oxidation, and phytoremediation. Although the system has not been tested on common POPs, Greenberg et al suggest that the combination of multiple techniques would speed up the rate and extent of remediation. In an eight-month case study in 2004 and 2005, the MPPS was able to remove 95 percent of polycyclic aromatic hydrocarbons (PAHs) from the soil. Because PAHs are also recalcitrant chemicals, this holds great promise for persistent organic pollutants (Greenberg et al. 2005).

The effects of the plant rhizosphere have been extensively studied, but developments in the last five years have presented new ideas. A 2001 study of PCBs in soil suggests that a combination of planting and amending soils would be a highly successful treatment. Flat pea, burr medic, and red canarygrass plants were planted in unamended soil (the control) or in soils amended with pine needles, biphenyl, or orange peels. The soils contained 50mg/kg of PCB and were tested over a 100-day period. Most treatment combinations of plants and an amendment resulted in higher bacterial counts and increased microbial activity. In comparison to unamended soil that was planted, the amended and planted soils increased PCB dissipation (Dzantor and Woolston 2001).

5. Future Outlook

Several factors make POP cleanup an arduous task. Education, cost, and regulatory issues are the major concerns that impact POPs and phytoremediation.

5.1. Education

The dangers of POPs are more widely known to people in developed countries than to those in developing and transitional economies. Increasing public awareness and basic education about the contaminants could ignite involvement and advocacy within these communities. Awareness and education also are a means of empowerment. As individuals learn about the dangers of the contaminants, they can share the knowledge with others. However, the lack of resources available to people in less developed countries can impact significantly how much of a difference education can make. Often, individuals in less developed areas are more focused on surviving day-to-day than on the possible long-term effects of hazardous chemicals.

The effects of education can be seen in the rise in labeling requirements for different chemicals. In the United States, as the public and lawmakers became more educated on the dangers of chemicals, regulation and restrictions (such as labeling requirements) increased. Also, as public awareness of pesticide dangers grew, people turned towards less risky options, fostering growth in the organic food industry. Since 1990 the market for organic food has grown 20 percent each year in direct correlation to increasing education and awareness at the time (PAN 1998). The Stockholm Convention also called for an increase in well trained specialists, educational

programs, and dissemination of information on alternative chemicals and solutions to POPs (Stockholm Convention 2005).

5.2 Cost

Cost is one of the main considerations when cleaning up POPs. Decontamination of POPs is generally difficult and costly. A detailed evaluation of the contaminants and the physical and chemical remediation methods available must be done to assess the applicability of such methods. Soil and groundwater remediation may be very expensive when using chemical methods, such as chemical oxidation, and may result in more dangerous products (Chaudhry et al. 2002). Also, traditional methods use electric power, which contributes significantly to their high cost. Other methods, such as thermal processes, are available but may not be efficient or affordable for countries that have limited access to resources and technologies. The FAO offers guidelines on prevention and disposal of obsolete pesticides in an effort to help countries minimize the need for expensive cleanup technologies the FAO has published guidelines on prevention and disposal (FAO 2005).

According to the FAO, the method chosen currently to clean up POPs in developing countries, high temperature incineration, can cost \$3,000 to \$4,500 per ton and may total as much as \$500million just to clean the most critically affected areas. Many countries do not have the capabilities required for this type of treatment. Because of this, such countries would have to repackage contaminants in a safe manner and ship them overseas to countries more capable of performing the incineration. The cost, repackaging, and transport of these contaminants are the prime reason for the investigation into the use of phytoremediation of POPs (FAO 2005).

Data collected in this report shows the cost of phytoremediation ranging from \$15,000 to \$694,000 in full-scale applications. Costs differ with the site size and operation and maintenance requirements. Past studies on phytoremediation involving other contaminants have shown that the phytoremediation mechanisms used also play a role in cost (see Table 5).

Table 5: Mechanisms and Cost

Mechanism	Estimated Cost
Phytoextraction	\$60,000-\$100,000
Rhizofiltration	\$2,000-\$6,000/thousand gallons of water
Phytostabilization	\$200-\$10,000/hectare
Phytodegradation	\$250,000
Hydraulic Control	\$250,000

Sources: ITRC 2001, EPA 2000

5.3. Regulatory Issues

Because POPs can be found anywhere in the world, cleaning them up requires international solutions and cooperation. International treaties such as the Stockholm Convention have been developed to control and phase out the use of POPs. The United States has signed, but not ratified, the Stockholm Convention which makes it difficult for new chemicals to be regulated. A list of countries that have ratified the Stockholm Convention, along with three other conventions that regulate POPs in connection with people, wildlife, and the environment, can be found at www.worldwildlife.org/toxics/pubs/treatyscorecard.pdf. Continuous collection of data and research is required so that new POPs can be evaluated and information can be shared across the globe (Stockholm Convention 2005; WWF 2005).

Overall acceptance of phytoremediation has grown in recent years and has led to an increase in its use. However, regulatory and policy issues related to several topics remain. They include:

- Disposal of contaminated plant material;
- Assessment of human health and ecological risk,
- Effects of genetically modified or non-native plants if used,
- Fate and transport of a contaminant to other media, and
- Criteria to determine effectiveness (ITRC 2001)

These issues are concern the effects of phytoremediation on the environment and health. As such, how they are resolved may impact, positively or negatively, the further acceptance and use of phytoremediation.

Other regulatory and policy issues can be found at the ITRC website (www.ITRCweb.org).

The data contained in this report indicate that although the field of phytoremediation continues to grow, more research must be done on phytoremediation of persistent organic pollutants. The information found on phytoremediation of DDT, PCBs, and atrazine demonstrate the potential use of the technology on other persistent contaminants, but they have not been investigated independently.

Information obtained on the abundance of POPs in developing and transitional countries indicate that phytoremediation has great potential for use. These countries are heavily burdened with POPs that are buried underground, in stockpiles, or in open dumps. Resources and technology are not readily available to aid these countries in cleaning up the contaminants, which makes a cost-effective and easily applicable technology like phytoremediation ideal.

Appendices

Appendix 1

Parties to the Stockholm Convention

As of May 24, 2005

(beginning with most recent signer)

- 100) Singapore – May 24, 2005
- 99) Honduras – May 23, 2005
- 98) Venezuela – April 19, 2005
- 97) Democratic Republic of the Congo –
March 23, 2005
- 96) Eritrea – March 10, 2005
- 95) Cyprus – March 7, 2005
- 94) Thailand – January 31, 2005
- 93) Argentina – January 25, 2005
- 92) Chile – January 20, 2005
- 91) Oman – January 19, 2005
- 90) United Kingdom of Great Britain
and Northern Ireland – January 17, 2005
- 89) Burkina Faso – December 21, 2004
- 88) Bulgaria – December 20, 2004
- 87) Qatar – December 10, 2004
- 86) Liechtenstein – December 3, 2004
- 85) European Community – November 16,
2004
- 84) Jordan – November 8, 2004
- 83) Romania – October 28, 2004
- 82) Latvia – October 28, 2004
- 81) Monaco – October 20, 2004
- 80) Albania – October 4, 2004
- 79) New Zealand – September 24, 2004
- 78) Kenya – September 24, 2004
- 77) Kiribati – September 7, 2004
- 76) China – August 13, 2004
- 75) Solomon Islands – July 28, 2004
- 74) Togo – July 22, 2004
- 73) Uganda – July 20, 2004
- 72) Portugal – July 15, 2004
- 71) Mauritius – July 13, 2004
- 70) Cook Islands – June 29, 2004
- 69) Tunisia – June 17, 2004
- 68) Brazil – June 16, 2004
- 67) Morocco – June 15, 2004
- 66) Barbados – June 7, 2004
- 65) Ecuador – June 7, 2004
- 64) Spain – May 28, 2004
- 63) The Former Yugoslav Republic of
Macedonia – May 27, 2004
- 62) Nigeria – May 24, 2004
- 61) Saint Kitts and Nevis – May 21, 2004
- 60) Australia – May 20, 2004
- 59) Slovenia – May 4, 2004
- 58) United Republic of Tanzania – April 30,
2004
- 57) Mongolia – April 30, 2004
- 56) Myanmar – April 19, 2004
- 55) Republic of Moldova – April 7, 2004
- 54) Paraguay – April 1, 2004
- 53) Djibouti – March 11, 2004
- 52) Chad – March 10, 2004
- 51) Philippines – February 27, 2004
- 50) France – February 17, 2004
- 49) Uruguay – February 9, 2004
- 48) Belarus – February 3, 2004
- 47) Côte d'Ivoire – January 20, 2004
- 46) Tuvalu – January 19, 2004
- 45) Azerbaijan – January 13, 2004
- 44) Yemen – January 9, 2004
- 43) Benin – January 6, 2004
- 42) Denmark – December 17, 2003
- 41) Armenia – November 26, 2003
- 40) Senegal – October 8, 2003
- 39) Papua New Guinea – October 7, 2003
- 38) Sierra Leone – September 26, 2003
- 37) Antigua and Barbuda – September 10,
2003
- 36) Mali – September 5, 2003
- 35) Dominica – August 8, 2003
- 34) Switzerland – July 30, 2003
- 33) Bolivia – June 3, 2003
- 32) Ghana – May 30, 2003
- 31) Egypt – May 2, 2003
- 30) Panama – March 5, 2003
- 29) Mexico – February 10, 2003
- 28) Luxembourg – February 7, 2003
- 27) Marshall Islands – January 27, 2003

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- 26) Ethiopia – January 9, 2003
- 25) Lebanon – January 3, 2003
- 24) Trinidad and Tobago – December 13, 2002
- 23) Botswana – October 28, 2002
- 22) Saint Lucia – October 4, 2002
- 21) South Africa – September 4, 2002
- 20) Finland – September 3, 2002
- 19) Japan – August 30, 2002
- 18) Austria – August 27, 2002
- 17) Democratic People's Republic of Korea – August 26, 2002
- 16) Czech Republic – August 6, 2002
- 15) Slovakia – August 5, 2002
- 14) Viet Nam – July 22, 2002
- 13) United Arab Emirates – July 11, 2002
- 12) Norway – July 11, 2002
- 11) Rwanda – June 5, 2002
- 10) Iceland – May 29, 2002
- 9) Liberia – May 23, 2002
- 8) Nauru – May 9, 2002
- 7) Sweden – May 8, 2002
- 6) Germany – April 25, 2002
- 5) Samoa – February 4, 2002
- 4) Netherlands - January 28, 2002
- 3) Lesotho – January 23, 2002
- 2) Fiji – June 20, 2001
- 1) Canada – May 23, 2001

Source: International POPs Elimination Network. 2005. <http://www.ipen.ecn.cz/index.php?1=en&z=print&r=viewtxt&id=60>

Appendix 2

Uses of POPs

Aldrin—In the 1950s, aldrin was used primarily to treat termites and beetles on a variety of crops, such as corn, potatoes, and cotton, as well as to guard wood structures. As a pesticide to treat soil insects, it has been frequently used to kill rice-water weevils, corn rootworms, wireworms, and grasshoppers.

Chlordane—Since 1945, chlordane has been used as an insecticide. Its major function was to control termites and insects birthed from the soil. Farmers used chlordane for many years as a pesticide on crops, such as corn, small grains, maize, fruits, nuts, cotton, sugarcane, etc. Chlordane also is used in livestock, home gardening, and control of fire ants near power transformers.

DDT—Perhaps one of the most infamous of the POPs, DDT was hailed by society as an effective insecticide in the 1930s. It was used to control vector-borne diseases, such as malaria and typhus, and some countries are still dependent upon it. DDT also has been effective on a variety of crops, especially cotton, but is widely restricted because of its adverse health and environmental effects.

Dieldrin—This pesticide has been used on cotton, corn, potatoes, and other crops. It also can be used for vector control, wood treatment, control of termites and textile pests, and mothproofing of wool products. Most uses for dieldrin are limited now to termite control.

Endrin—This pesticide has been used in agriculture on crops, such as cotton, sugarcane, grains, apples, and ornamentals. Since its introduction in 1951, Endrin has been used as a rodenticide and insecticides for controlling mice, voles, and insects that invade orchards and fields. Endrin also was used to control birds. Its use has been banned or restricted in many countries since the 1980s.

Heptachlor—The main function of heptachlor is to treat termites and soil insects. Other uses include control of malaria, cotton insects, and crop pests. Despite its many uses, heptachlor has been banned by many countries, and only a few uses, such as underground control of termites, are permitted today.

HCB—This is an insecticide, industrial chemical, and a chemical byproduct. When introduced in 1945, it was used as a fungicide. HCB was a means of treatment for the seeds of onions, wheat and sorghum. The chemical also was used as a manufacturing intermediate and solvent in the production of synthetic rubber, PVC plastics, dyes, etc. While these uses have been banned or severely restricted in many countries, HCB is still produced as a byproduct in the manufacturing of industrial chemicals and the burning of municipal waste.

Mirex—Mirex has a variety of functions as an insecticide. Dominant uses were for killing fire ants, leaf cutter ants, harvester termites, Western harvester ants, and mealy bug of pineapple. Mirex also has been widely used as a fire retardant in rubber, paper, plastics, and paint.

Toxaphene—After its introduction to the market in 1949, toxaphene was used most heavily in the 1970s. Toxaphene has been used mainly to kill insects on cotton, fruits, nuts, cereal grain, and vegetables; control ticks and mites on livestock and poultry; and even to kill unwanted species of fish. Toxaphene is now banned or severely restricted in many countries.

PCBs—PCBs were first manufactured in 1929. Several countries produced them for export. PCBs, which are industrial chemicals and chemical byproducts, had a variety of uses. Dominant usage was in transformers, plastics, flame retardants, heat transfer and hydraulic systems, and in carbonless copy paper.

Dioxins and Furans— The production of chlorinated solvents and other chemicals discharge dioxins and furans into the environment. Dioxins and furans are produced through the incineration of medical, municipal, sewage, wood, coal, and hazardous waste; paper and pulp bleaching; and the refining and smelting of metals. Burning in open fields and forest fires produce many dioxins that are deposited on trees and in fields to circulate through the atmosphere. Many countries incinerate wastes, and dioxins and furans continue to be discharged.

Source: Ritter 1995; FAO 2005; PAN 1998

Appendix 3

Preliminary List of Countries with
Known Obsolete Pesticide Stocks

Countries in Africa	Pesticide stocks total (tons)	Disposed of
Algeria	207	
Benin	421	
Botswana	18,247	
Burkina Faso	75	
Burundi	169	
Cameroon	225	
Cape Verde	43	
Central African Republic	238	
Dem. Rep. of Congo	591	
Rep. of Congo	2	
Cote d'Ivoire	828	821
Egypt	591	
Equatorial Guinea	146	
Eritrea	223	
Ethiopia	3,401	
Gambia	21	21
Ghana	72	
Guinea-Bissau	9	9
Guinea-Conakry	47	
Kenya	56	
Libya	44	
Madagascar	64	64
Malawi	111	
Mali	13,761	
Mauritania	297	200
Morocco	2,265	
Mozambique	443	
Namibia	245	202
Niger	151	
Nigeria	22	

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Rwanda	451	
Sao Tome and Principe	3	
Senegal	289	110
Seychelles	12	12
Sierra Leone	7	
South Africa	603	603
Sudan	666	
Swaziland	9	9
Tanzania	1,136	57
Togo	86	
Tunisia	882	
Uganda	254	90
Zambia	360	360
Zanzibar	280	280
Zimbabwe	27	
Total	48,081	2,838
-		
Countries in the Middle East	Pesticide stocks total (tonnes)	Disposed of
Iran	1,139	
Iraq	232	
Kuwait	32	
Lebanon	189	10
Qatar	5	5
Saudi Arabia	241	
Syria	327	
Yemen	1,802	262
Total	3,967	277

Source: FAO.2001<. <http://www.fao.org/NEWS/2001/010505-e.htm>> Accessed on August 3, 2005.

Appendix 4

Case Studies

Following is a summary of the case studies included in this report. More detailed information about each of the studies begins on the next page.

Summary:

Type	Number of Studies	Contaminants
Bench-Scale	8	Atrazine, DDT & metabolites, HCB, PCB, chlorinated benzene
Greenhouse and Plot	16	DDT & metabolites, PCBs, atrazine, HCH, alachlor, chlordane, metolachlor
Full-Scale	13	PCBs, atrazine, alachlor, metolachlor, dieldrin, aldrin, HCB, DDT

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Bench-Scale Studies:

No.	Study Title/ Site Name	Project Date	Contaminant	Media	Vegetation	Mechanisms	Cost	Concentration Levels	Results	Lessons/ Comments	Involved Parties/ References
1	<i>Growth of PCB-Degrading Bacteria on Compounds from Photosynthetic Plants</i>	1994	PCB	Soil	Plant compounds—naringin, phloridizin, catechin, chrysin, maclurin, myricetin	Rhizodegradation (RD)		80-100% of PCBs were metabolized by H850 bacteria on naringin.	To sustain bacteria and promote microbial activity, naringin was best.	Studied the ability of certain plants to support PCB-degrading bacteria	University of Oklahoma Donnelly et al, 1994
2	<i>Phytoremediation: Plant Uptake of Atrazine and Role of Root Exudates</i>	1996 (80-day period)	Atrazine	Soil (sand and silt loam)	Hybrid poplars trees	Phytoextraction (PE)	\$20,000/ hectare	Uptake in sand was 94% at 9 days; uptake in silt-loam was 29.2% at 80 days	Direct uptake was greatest in sand.		University of Iowa Burken and Schnoor 1996
3	<i>Uptake and Metabolism of Atrazine by Poplar Trees</i>	1997	Atrazine	Soil (sand and silt-loam)	Poplar trees	PE		For trees in sand, 71 (+/- 8)% uptake at 13 days; for silt-loam, 27.8% at 52 days and 29.2 % of total applied at 80 days			University of Missouri Burken and Schnoor, 1997
4	<i>Enhancing Dissipation of Aroclor 1248 (PCB) Using Substrate Amendment in Rhizosphere Soil</i>	2001 (100-day period)	PCB	Soil	Burr medic, red canary grass, and flat pea	RD and Phytodegradation (PD)		Highest amount, 32.7 (+/- .3)% was recovered by flat pea; recovery levels in amended soil ranged from 20.5% to 39.2%	Highest PCB dissipation was in planted and amended soils.		University of Maryland Dzantor and Woolston, 2001
5	<i>Plant Assisted Volatilisation of Semi-Volatile, Persistent Organic Pollutants</i>	2005	Chlorinated benzenes	Soil		Phytovolatilization (PV) and PD			Volatilisation occurs directly from the soil and not through plant tissue		University of Aberdeen, UK Baughn and Meharg, 2005
6	<i>Conjugation of</i>	2005	Atrazine		Vetiver				Atrazine was		Swiss

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No.	Study Title/ Site Name	Project Date	Contaminant	Media	Vegetation	Mechanisms	Cost	Concentration Levels	Results	Lessons/ Comments	Involved Parties/ References
	<i>atrazine in vetiver (Chrysopogon zizanioides) grown in hydroponics</i>								transformed primarily into polar compounds.		Federal Institute of Technology Lausanne, Switzerland Marracci et al, 2005
7	<i>Uptake and degradation of DDT by hairy root cultures of Cichorium Intybus and Brassica Juncea</i>	2005 (10-day period)	DDT and metabolites	Soil	Hairy root cultures of cichorium intybus and brassica juncea	RD		14-C DDT in roots decreased from 77% to 61% over 10 days.	DDT was degraded to its metabolites and other unknown compounds.	Rate of <i>in situ</i> degradation was higher in initial stages.	Central Food Technological Research Institute Suresh et al, 2005
8	<i>Enhancement of Reductive Dechlorination of Aged Hexachlorobenze in Planted Sediment</i>	2005 (125-day period)	HCB	Sediment	Typha latifolia and Phragmites communis	PD and RD		After 125 days, no HCB was detected.	Plant species increase the degradation of HCB.	Phragmites was best at improving microbial activity.	Louisiana State University Ma and Pardue, 2005

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Greenhouse and Plot Studies:

No.	Study Title/ Site Name	Project Date	Contaminant	Media	Vegetation	Mechanisms	Cost	Concentration	Results	Lessons/ Comments	Involved Parties/ References
1	<i>Fate of alachlor and atrazine in a riparian zone field site</i>	1991	Atrazine and alachlor	Soil	Corn and poplars (atrazine); corn (alachlor)	PE		3.6 (+/- 1.3)% uptake of atrazine in poplars and 5.5 (+/- 1.8)% in corn; 12.5 (+/- 4.5)% uptake of alachlor in corn	Overall, corn had the highest uptake.	Amounts of uptake are directly related to water volume transpired.	U.S. EPA Regions 7 and 8, University of Iowa Peterson and Schnoor, 1992
2	<i>Concurrent plant uptake of heavy metals and persistent organic pollutants from soil</i>	2000-2002	Weathered chlordane	Soil	Zucchini, lettuce, pumpkin, cucumber, white lupine, thistle, spinach and tomato	PE		Initial concentration in soil was 3,000-6,000 ng/g. Bioconcentration factor (BCF) for zucchini was 0.38, for lettuce, 0.11.			Connecticut Agricultural Experiment Station, New Haven, CT, USA Mattina et al, 2003
3	<i>Atrazine and phenanthrene degradation in grass rhizosphere</i>	2000	Atrazine	Soil	Ryegrass, tall fescue, crested wheatgrass, Sudan grass, and switch grass	PD			Most rapid degradation was in rhizosphere soil. Overall rates were very low.	Sudan grass and switch grass were the only species to survive.	University of Delaware Fang et al, 2001
4	<i>Tracking chlordane compositional and chiral profiles in soil and vegetation</i>	2001 (90-day period)	Chlordane	Soil	Zucchini	PE		Rhizosphere soil had 14% reduction of chlordane concentration from the bulk soil.	Roots had maximum chlordane levels; fruit had minimum.	Roots excrete substances that make contaminants more available.	Connecticut Agricultural Experiment Station, New Haven, CT White et al, 2001
5	<i>Jones Island Confined Disposal Facility, WI</i>	2001	PCB	Soil	Clover, corn, willow	RD	\$ 5,360.01 (willow), \$1,960.01 (corn)		Sediments were more aerobic because of plants, and had a negative effect on remediation.		U.S. EPA, Purdue University Euliss, 2005; EPA, 2003b; EPA, 2003a

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No.	Study Title/ Site Name	Project Date	Contaminant	Media	Vegetation	Mechanisms	Cost	Concentration	Results	Lessons/ Comments	Involved Parties/ References
6	<i>The Use of Native Prairie Grasses To Degrade Atrazine and Metolachlor in Soil</i>	2003	Atrazine and metolachlor	Soil	Native prairie grasses: big bluestem, yellow indidan, switchgrass			Atrazine in soil, 100 µg/g; metolachlor in soil, 25 µg/g	Metolachlor decreased significantly.		Karthikeyan et al, 2004
7	<i>Subspecies-level variation in the Phytoextraction of weathered p,p'-DDE by Cucurbita pepo</i>	2003	DDE	Soil	Cucurbita pepo ssp texana, cucurbita pepo ssp pepo	PE		Pepo extracted 0.301%; texana extracted 0.065%.	C. pepo extracted highest amounts of DDE.	C. pepo extraction is due to low molecular weight of organic acid exudation.	Connecticut Agricultural Experiment Station, New Haven, CT White et al, 2003
8	<i>Monitoring Plant Species Grown In Pesticide Contaminated Soil (Kazakhstan)</i>	2003 (3-year study)	HCH, DDT, DDE, DDD	Soil	Several species from Asteraceae and Chenopodaceae families	PE	Research Grant for \$260,000	17 of 123 plant species were found to be pesticide-tolerant.	HCH isomers were found most in aboveground tissues; DDT was mainly in plant root.	Annual plant species accumulated more than biannuals.	Nurzhanova et al, 2005
9	<i>Rhizoremediation of PCBs: Mechanistic and Field Investigations (Czech Republic)</i>	2003	PCBs	Soil	Ash, Austrian pines, black locust, willow trees	RD			Black locust and Austrian pine enhance PCB degradation.		Leigh et al, 2003
10	<i>Uptake of Weathered DDT in Vascular Plants: Potential for Phytoremediation (Canada)</i>	2004	DDT and metabolites	Soil	Zucchini, tall fescue, rye grass, alfalfa, pumpkin	PE		Initial in Soil: 3,700 ng/g and 150 ng/g; uptake by zucchini roots: 2,043ng/g; uptake by pumpkin shoots: 57,536 ng/g		Fescue and alfalfa were not successful.	Royal Military College of Canada Lunney et al, 2004

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No.	Study Title/ Site Name	Project Date	Contaminant	Media	Vegetation	Mechanisms	Cost	Concentration	Results	Lessons/ Comments	Involved Parties/ References
11	<i>Differential Bioavailability of Field-weathered p,p'-DDE to Plants of the Cucurbita and Cucumis Genera</i>	2004	DDE	Soil	Varieties of squash, pumpkin, zucchini, and melon	PE	N/A	Initial in Soil: 161 ng/g; uptake by squash roots: 2910 ng/g; BCF for squash/pumpkin was 16.	Goldrush summer squash and Howden pumpkin extracted the most.	Most of the pollutants extracted were in the shoots.	Connecticut Agricultural Experiment Station, New Haven, CT White, 2002
12	<i>In Situ Phytoextraction of PCBs from Soil: Pilot-Scale Field Trial</i>	2004	PCBs	Soil	Pumpkin, tall fescue, and spreading oval sedge	PE		Pumpkin: shoots, 16.8 µg/g; roots, 730 µg/g Tall fescue: shoots, 6.2 µg/g; roots, 440 µg/g	Other plants were tested, but pumpkin and tall fescue were best.		Royal Military College of Canada Whitfield, 2005; Whitfield et al, 2005
13	<i>Phytoextraction of Recalcitrant Organic Pollutants from Soil by Agricultural Species</i>	2004	PCBs, p,p'-DDE, chlordane	Soil	Cucurbita pepo	PE			Up to 2.4% of contaminants extracted from soil.		Connecticut Agricultural Experiment Station, New Haven, CT White and Mattina, 2004
14	<i>Phytoextraction of Organo Chlorines (PCBs and DDT) Greenhouse Treatability and Pilot-Scale Field Studies, Canada</i>	2004	PCB, DDT	Soil	Rye grass, tall fescue, common sedge, alfalfa, zucchini, and pumpkin	PE		In soil, high levels were 10,000 ppm PCBs and 4,500 ppb DDT; low levels were 110 ppm PCBs and 100 ppb DDT.	Zucchini and common sedge plants were best for PCBs, pumpkin, and zucchini plants best for DDT.		Royal Military College of Canada Zeeb et al, 2004
15	<i>Uptake of weathered p,p'-DDE by plant species effective at accumulating soil elements</i>	2005	DDE	Soil	Rye, vetch, mustard, canola, pigeon pea, clover, peanut, white lupine	PE	N/A	Amounts extracted ranged from 0.06% (white lupine) to 0.22% (clover and vetch).	Extracted amounts doubled in certain plants with nitrogen, potassium, or both being added.	Effects of additions to soil are species-specific and vary.	Connecticut Agricultural Experiment Station, New Haven, CT White et al, 2005

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No.	Study Title/ Site Name	Project Date	Contaminant	Media	Vegetation	Mechanisms	Cost	Concentration	Results	Lessons/ Comments	Involved Parties/ References
16	<i>Phytotechnologies for Management of Radionuclide Obsolete Pesticide Contaminated Soil in Ukraine</i>	2005	DDT, HCH, atrazine	Soil	Vegetable marrow and bean plants	PE		In soil, 2.2- 1,696.5 µg/kg DDT, DDE, and DDD; 1.5-2,030.6 µg/kg HCH and its isomers; 692.2 µg/kg PCB; 400 µg/kg atrazine	Plants were able to accumulate and degrade DDT.		Institute of Agroecology and Biotechnology of Ukrainian Academy of Agrarian Sciences Moklyachuk et al, 2005

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Full-Scale Studies

No.	Study Title/ Site Name	Project Date	Contaminant	Media	Vegetation	Mechanisms	Cost	Concentration	Results	Lessons/ Comments	Involved Parties/ References
1	<i>Polychlorinated Biphenyl Accumulation in Tree Bark and Wood Growth Rings</i>	1987	PCB	Soil	Black walnut, white oak, and tulip poplar	PE		Walnut: 12ng/g Oak: 0.36ng/g Poplar: 56ng/g		Concentrations in bark are likely related to atmospheric concentrations.	Indiana University Meredith and Hites, 1987
2	<i>Okonee, IL</i>	1987-1996 (GW) 1987-1990 (Soil)	Atrazine, alachlor, metolachlor	GW and Soil	Corn, alfalfa, hybrid poplars grasses	RD		All groundwater contaminants were above 1,400 ppb in 1987. In 1996, all were below 400 ppb. In soil, all fell well below 50 ppm by 1990.	All levels decreased after technology was applied.		Applied Natural Sciences Applied; Phytoremediation, 2000e
3	<i>Whitewater, WI</i>	1992	Herbicides/pesticides	GW	Grass, hybrid poplars, legumes	Hydraulic control (HC)					Applied Natural Sciences Phytoremediation, 2000f
4	<i>Cantrall, IL</i>	1992-2005	Atrazine, alachlor	GW and Soil	Hybrid poplars	PD, Phytostabilization (PS), and RD	\$20,000	Atrazine & alachlor are present but not migrating into soil.	Atrazine and alachlor are no longer prime contaminants.	Site is about one acre, planted with about 240 trees that are now approximately 50 feet high.	State of Illinois Voluntary Program and Thomas Consultants Thomas, 2005; Thomas; Phytoremediation, 2000a
5	<i>Clarence Coop-Martelle Plant, IA</i>	1993	Atrazine, herbicides	GW and Soil	Hybrid Poplar, grasses	PE, PS, RD	\$ 15,000				Iowa Department of Natural Resources and Ecolotree Phytoremediation 2000b

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No.	Study Title/ Site Name	Project Date	Contaminant	Media	Vegetation	Mechanisms	Cost	Concentration	Results	Lessons/ Comments	Involved Parties/ References
6	<i>Matoon, IL</i>	1994	Alachlor	Soil	Hybrid poplars						Voluntary & Thomas Consultants Phytoremediation, 2000d
7	<i>Indianapolis, IN</i>	1995	Atrazine, alachlor	GW	Hybrid poplars						Voluntary and Thomas Consultants Phytoremediation, 2000c
8	<i>Fort Wainwright, AK</i>	1997-2002	Dieldrin, aldrin, DDT	Soil	Felt leaf willow	PE, RD			Aldrin decreased; dieldrin was unchanged.		Soderlund, 2005; Gusmano, 2005; EPA, 1997, 1999
9	<i>Tibbets Road, NH</i>	1998-2015	PCB	GW and Soil	Hybrid poplars, understory grasses	HC, PE	\$40,000				PRPs, Federal and State Oversight EPA, 2004; Luce, 2005
10	<i>Aberdeen Pesticide Dumps, Superfund Site NC</i>	1999	Dieldrin, HCB	GW and Soil	Hybrid poplars, groundcover grasses	RD, PD, HC	\$450,000			Final inspections conducted in May 2000 and March 2001.	PRPs, Federal and State Oversight EPA, 2003a
11	<i>Successful Full Scale Phytoremediation of PCB and TPH Contaminated Soil</i>	2001-2003	PCB	Soil	Red mulberry trees, Bermuda grass	PE	\$250,000	Levels averaged 100-225ppm at the beginning, 2-8 ppm at the end.	Over 200 samples were taken, and the contaminant levels decreased significantly.	Site was about two acres, and trees were planted at a depth of about three feet.	Freelance Consulting Services Hurt, 2005; Hurt, 2005
12	<i>Combustion, Inc., LA</i>	2002	PCB	GW	Poplars, native willows, eucalyptus	HC, PV, RD	\$694,000		No data yet	Estimated 5-year review date is March 2011. Phytoremediation upgrades were done in April 2005.	PRPs with Federal oversight EPA, 2005a; Coltrain, 2005

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No.	Study Title/ Site Name	Project Date	Contaminant	Media	Vegetation	Mechanisms	Cost	Concentration	Results	Lessons/ Comments	Involved Parties/ References
13	<i>Etobicoke, Ontario, Canada</i>	2004	PCB	Soil	Pumpkin, tall fescue, spreading oval sedge	PE		Concentration levels of plants are lower than concentrations in soil.		Contamination is low.	Royal Military College of Canada Whitfield, 2005; Whitfield et al, 2005

Appendix 5

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