# Bioremediation of Pesticides

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**ABSTRACT**

Bioremediation of hazardous wastes is a relatively new technology that has undergone more intense investigation as of recent decades. This process is focused on destroying or immobilizing toxic waste materials. Pesticides are a common hazard around the world, as these chemicals are leaching into soils, groundwater and surface water and creating health concerns in many communities. The persistence of pesticides makes their removal and detoxification a more urgent undertaking. The bioremediation of pesticides can be divided into two broad categories: in-situ and ex-situ treatment. Both methods have significant advantages and disadvantages.

**KEYWORDS**
Bioremediation, pesticide, treatment, organic, pollutants, contamination, microorganisms

## INTRODUCTION

Contamination of surface water, ground water and soils can result in devastating consequences for plant and animal life that is near the source. In recent years, the negative effects of human waste products on the environment have been recognized and many societies are now seeking to reverse the damage. A few of the many solutions that have been and are being investigated are containment, incineration, chemical treatment, volatilization, phytoremediation and bioremediation (Fragoeiro, 2005). This paper will focus on bioremediation as a solution to the worldwide contamination problem.

## BIOREMEDIATION HISTORY AND USES

*Bioremediation Definition and History*
Bioremediation is described as the use of microorganisms to destroy or immobilize waste materials (Shanahan, 2004). This process of detoxification targets the harmful chemicals by mineralization, transformation, or alteration (Shannon and Unterman, 1993). For centuries, civilizations have used natural bioremediation in wastewater treatment, but intentional use for the reduction of hazardous wastes is a more recent development.

Modern bioremediation and the use of microbes to consume pollutants are credited, in part, to George Robinson (US Microbics, 2003). He used microbes to consume an oil spill along the coast of Santa Barbara, California in the late 1960s. Since the 1980s, and bioremediation of oil spills and other environmental catastrophes, biological degradation of hazardous wastes has received more consideration (Shannon and Unterman, 1993).

*Objectives of Bioremediation*
The process of biologically degrading wastes can be applied to many different types of wastes such as wastewater, petroleum wastes, solvents, and pesticides. Figure 1 illustrates the process of treatment via microbes. Bioremediation as a whole is focused on accomplishing the following objectives, regardless of the waste to be degraded:

- Oxidation of organic contaminants
- Biotransformation of organic chemicals into smaller, less toxic constituents
- Reduction of highly electrophilic halo- and nitro- groups by transferring electrons from the contaminant (termed the electron donor) to an electron acceptor to gain energy (Rockne and Reddy, 2003)

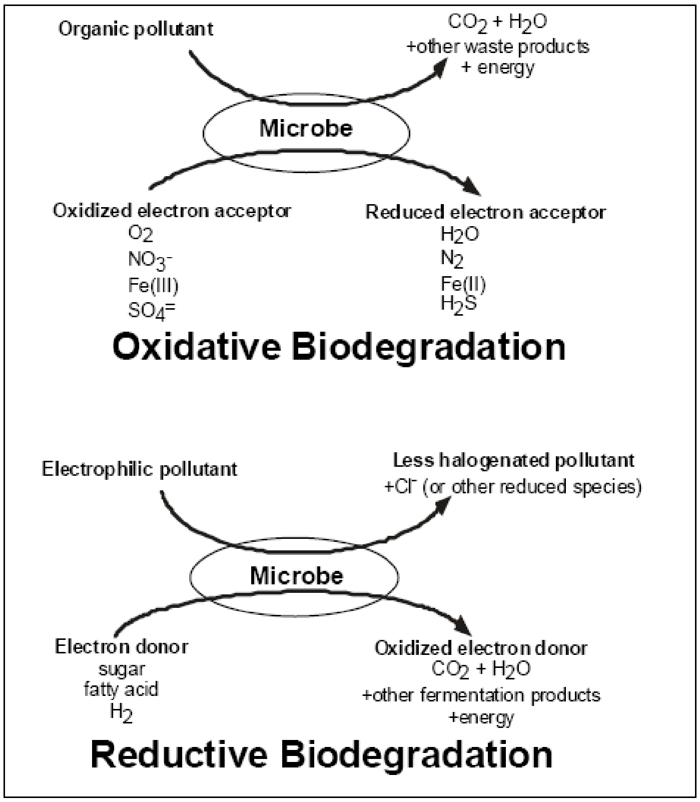

Figure 1: General Process of Organic Contaminant Degradation (Rockne and Reddy, 2003)

**PESTICIDE INFORMATION**

*Description of Pesticides*
The United States Environmental Protection Agency (EPA) defines a pesticide as any substance or mixture of substances intended for preventing, destroying, repelling or mitigating any pest (USEPA, 2006). Pesticides can be broken into subcategories of herbicides, insecticides, fungicides, virucides, and others according to the targeted pest. In this paper, all pesticides will be discussed as one category, though subcategories may be mentioned.

Pesticides can be classified by their sources. These classifications include chemical pesticides, biopesticides, antimicrobials, and pest control devices (USEPA, 2006). Biopesticides contain naturally occurring materials such as plants, animals, bacteria, and minerals (USEPA, 2006). Antimicrobials are pesticides that are used to destroy harmful microorganisms. The final category, pest control devices, includes instruments intended for trapping, destroying, repelling, or mitigating any pest through only physical or mechanical means (USEPA, 2006). This paper will focus solely on chemical pesticides.

Pesticides are classified by structure. Some examples of pesticide structures may be found in Figure 2. These structural classifications include organochlorine (OC), organophosphorus (OP), carbamate, and nitrogen-based pesticides, among others (Vaccari et al, 2006). Table 1 shows these categories of pesticides and some examples of each category.

Table 1: Types of Pesticides and Examples (Vaccari et al, 2006)

| Pesticide | Examples |
|---|---|
| Insecticide | |
| Organophosphorus | Diazinon, dichlorvos, dimethoate, malathion, parathion |
| Carbamate | Carbaryl, propoxur, Aldicarb methiocarb |
| Organochlorine | DDT, methoxychlor, toxaphene, mirex, Kepone |
| Cyclodienes | Aldrin, chlordane, dieldrin, endrin, endosulfan, heptachlor |
| Herbicides | Chlorophenoxy acids, hexachlorobenzene (HCB) |
| Nitrogen-based | Picloram, Atrazine, diquat, paraquat |
| Organophosphates | Glyphosate (Roundup) |
| Fungicide | |
| Nitrogen-containing | Triazines, dicarboximides, phthalimide |
| Wood preservatives | Creosote, hexachlorobenzene |
| Antimicrobial | Chlorine, quaternary alcohols |
| Botanicals | Perethrin, permethrin |

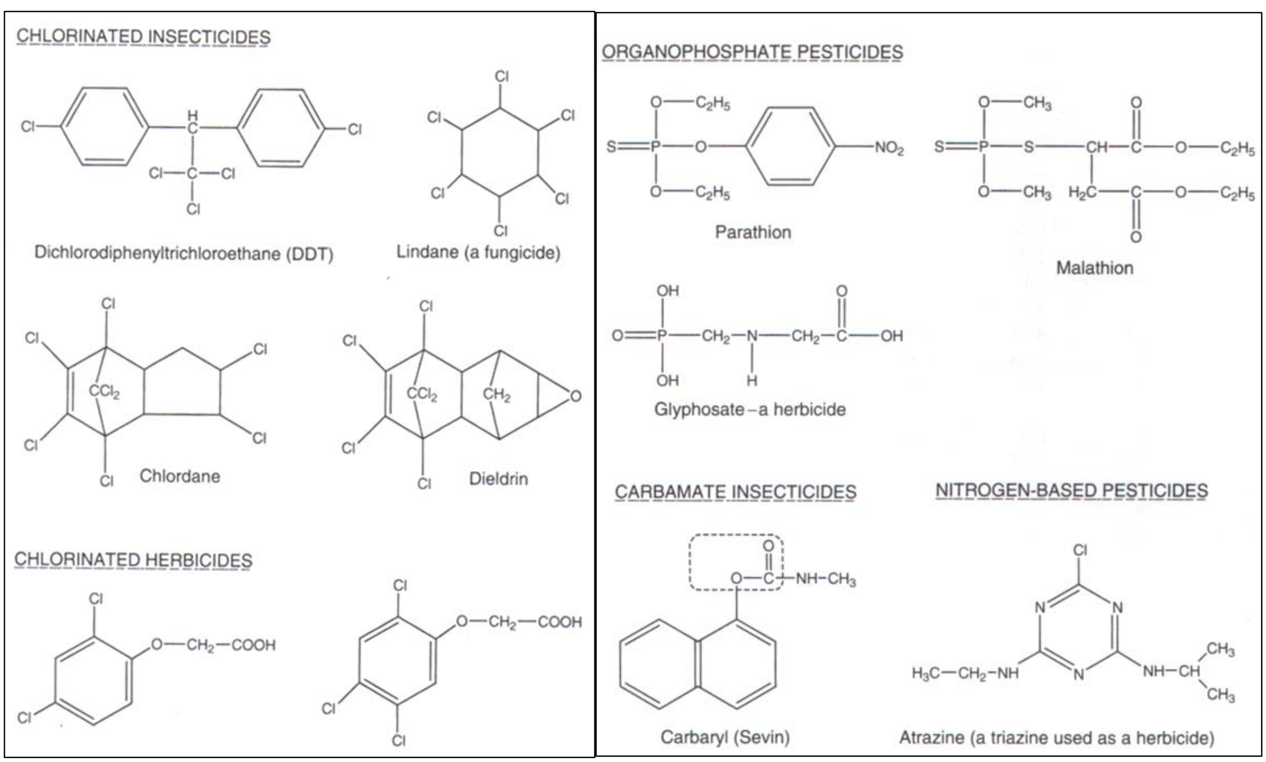


Figure 2: Common Pesticides Classified by Structure (Vaccari et al, 2006)

*Pesticide Concerns*
Pesticides are toxic to many organisms and pose a threat to the safety of ground and surface water. The contamination of surface and ground water with pesticides produces many adverse effects on the surrounding ecosystem. Many insecticides function by impeding normal nervous system functions. OC and OP compounds stimulate the nervous system and cause tremors, irritability and convulsions (Vaccari et al, 2006). Chronic exposure to organophosphates can cause destruction of nerve fibers (neuropathy) as well as muscle tissue damage (myopathy) (Vaccari et al, 2006). Table 3 shows more negative health effects of common pesticides.

Organochloride insecticides have been found to accumulate in human adipose tissue. Prolonged exposure to OC insecticides also cause convulsions, a hyperexcitable state of the brain, and cardiac arrhythmiatic symptoms.

Organochlorine pesticides create a distinct issue for environmental engineers and scientists due to biomagnification. Biomagnification is the increase in toxic substance with increasing trophic levels. For example, Figure 3 shows the biomagnifications of two pesticides through increasing trophic levels.

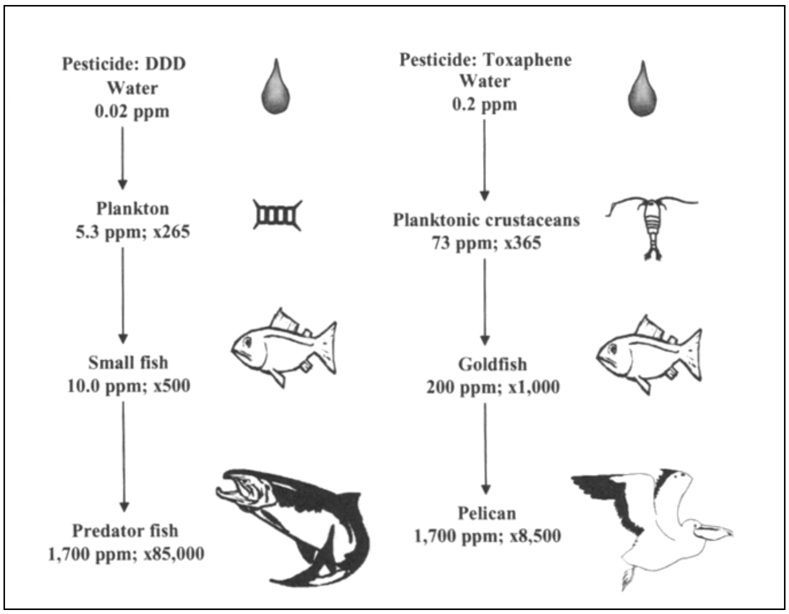

Figure 3: Biomagnification of Toxic Chemicals (Vaccari et al, 2006)

Due to the toxicity and biomagnification of OC compounds, these pesticides are mostly avoided in agricultural communities. Also, it has been found that by using OC insecticides, for example, the biomagnification resulted in an increased pest problem. This result occurred due to the biomagnification of the toxins, which were more harmful to the pest predators needed to control the pests. (Vaccari et al, 2006)

Table 3: Facts About Common Pesticides (Green and Hoffnagle, 2004)

| Pesticide | Molecular formula | Molecular weight | Density (g/m L ) | Aqueous Solubility (mg/L) | Log Kow | Persistence (Half-life) | Health Effects |
|---|---|---|---|---|---|---|---|
| Alachlor | 22014 Cl N O HC | 269.8 | 1.133 | 242 | 2.92 | 8 days | Effects on liver, spleen, kidney, iris, lung effects for long (6+ month) exposures |
| Aldrin | 6812 ClHC | 364.93 | 1.6 | 0.017 | 6.5 | 20 days to 1 year | Nervous system effects. Probable carcinogen. Large doses: convulsions, death. Moderate doses: dizziness, headaches, vomiting, uncontrolled muscle movement. |
| Atrazine | 5146 ClN HC | 215.7 | 1.187 | 70 | 2.68 | 60 to 100 days | Acute: abdominal pain, diahrrea, skin and mucous membrane irritation (low levels); incoordination, muscle spasms, hypothermia, hypoactivity, prostration, convulsions, death (higher does). Chronic: respiratory distress, limb paralysis, structural/ chemical |
| Chlordane | 8610 ClHC | 409.78 | 1.6 | 0.056 | 6 | 4 years | Nervous system, digestive system, liver effects. Headaches, irritability, confusion, weakness, vision problems, vomiting, stomach cramps, diarrhea, and jaundice for lower doses. Higher doses: convulsions and death. |
| Dichlorodiphe nyltri-chloroethane (DDT) | 5914 ClHC | 354.49 | 1.55 | 0.0055 | 6.19 | 2 to15 years | Nervous system effects (tremors, seizures); probable carcinogen |
| Dieldrin | O Cl HC 6812 | 380.92 | 1.75 | 0.2 | 5.48 | Up to 7 years | Nervous system effects. Probable carcinogen. Large doses: convulsions, death. Moderate doses: dizziness, headaches, vomiting, uncontrolled muscle movement. |
| Endrine | O Cl HC 6812 | 380.92 | 1.7 | 0.26 | 5.2 | Up to 12 years | Nervous system effects (large doses can cause severe central nervous system injury, convulsions, death; smaller doses can cause headaches, confusion, nausea, vomiting, and convulsions); birth defects |
| Heptachlor | 7510 ClHC | 373.32 | 1.58 | 0.18 | 5.47-6.10 | 0.4 to 2 years | Nervous system damage, liver and adrenal gland damage, tremors |
| Hexachlorobenzene (HCB) | 66ClC | 284.81 | 2.044 | 0.005 | 5.73 | 2.7 to 7.5 years | Damage to liver, thyroid, nervous system, bones, kidneys, blood, and immune systems; reasonably anticipated to be carcinogen |

**PESTICIDE BIOREMEDIATION METHODS**

The dangers of pesticide contamination in soils and groundwater lead to the great need of remediation. In some cases it has been found that intrinsic bioremediation can occur. At these sites, the microbes needed for bioremediation are already present in the soil or groundwater. However, naturally occurring chemical degradation is typically not a process that is completed within acceptable timeframes (Vaccari et al, 2006). Table 4 shows the requirements for soil bioremediation. In cases where intrinsic bioremediation is not adequate, engineered options that better control these conditions are available. There are two main categories of bioremediation methods: ex-situ and in-situ treatment. Both categories will be addressed and compared.

Table 4: Requirements for Soil Bioremediation (Shanahan, 2004)

| **Environmental Factor** | **Optimum Conditions** |
|---|---|
| Available soil moisture | 25-85% water holding capacity |
| Oxygen | >0.2 mg/L DO, >10% air-filled pore space for aerobic degradation |
| Redox potential | Eh > 50 millivolts |
| Nutrients | C:N:P = 120:10:1 molar ratio |
| pH | 5.5 to 8.5 |
| Temperature | 15 - 45°C |

*Ex-situ Bioremediation*

In some cases, contaminated soils and water are best treated after being removed from the contamination site. This act of removing and then treating is known as ex-situ treatment. The most common processes of ex-situ treatment are pump-and-treat, biopile treatment and land farming.

The pump-and-treat process is specifically designed to remediate contaminated groundwater. In this process, the contaminated water is removed from the ground and sent to an engineered treatment system. The treatment can occur via activated sludge, a trickling filter, rotating biological contactors, and ion exchange, among other possible systems (FRTR, 2006).

Landfarming, as other ex-situ treatment methods, involves the excavation and relocation of the contaminated media. The soil is tilled periodically to aerate the waste and remix the active microbes (Vaccari et al, 2006). In this process, several soil conditions are monitored to ensure a high rate of degradation. These criteria include, but are not limited to, moisture content, aeration and pH (FRTR, 2006). Throughout the bioremediation process, moisture and nutrients may be added to the soil as needed, and the pH can be controlled by adding crushed limestone or lime (FRTR, 2006). A typical landfarming operation is shown in Figure 4.

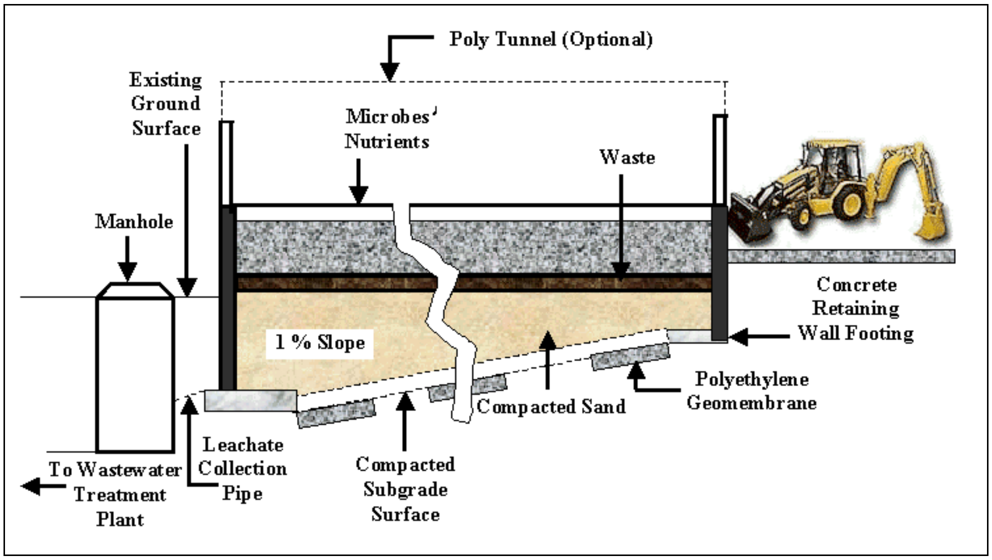

Figure 4: Typical Landfarming Treatment Unit (FRTR, 2006)

Ex-situ bioremediation generally requires a shorter amount of time to be completed than in-situ treatment (FRTR, 2006). Furthermore, ex-situ treatment is easier to control due to the possibility of continuous mixing during treatment. On the other hand, the ex-situ method also requires excavation and a possible increase in labor costs.

Some limitations of ex-situ bioremediation drastically affect the feasibility of using this technology. In all ex-situ treatments discussed, a large amount of space is required for treatment. In urban areas, this is a viable concern. Volatile contaminants must be either contained or pretreated, as they may volatilize into the air if not monitored, and may cause air pollution (FRTR, 2006).

*In-situ Bioremediation*
In-situ, or in place, treatment can be conducted through several different mediums. One of these mediums is fungi as a degrader of pesticides.

The application of white rot fungi for use in pesticide bioremediation has been extensively studied in recent years. In its natural environment, white rot fungi lives on woody tissues that contain lignin, a recalcitrant compound (Fragoeiro, 2005). The white rot fungi contain enzymes necessary to degrade lignin, as well as other toxic and recalcitrant compounds. In lab testing, it has been found that this fungi is capable of degrading certain pesticides 45-75% more effectively than control samples (Fragoeiro, 2005).

Bioventing is another in-situ treatment method for the biodegradation of pesticides (Vaccari et al, 2006). For this method of treatment, injection wells are constructed at the location of contamination. Figure 5 shows a typical bioventing operation. In bioventing, air is injected at a low rate, to supply just enough oxygen to maintain bioremediation (Shanahan, 2004). Nutrients and water are generally provided to replace microbial losses throughout the remediation process (Vaccari et al, 2006). Nitrogen and phosphorous are two commonly added nutrients (Rockne and Reddy, 2003).

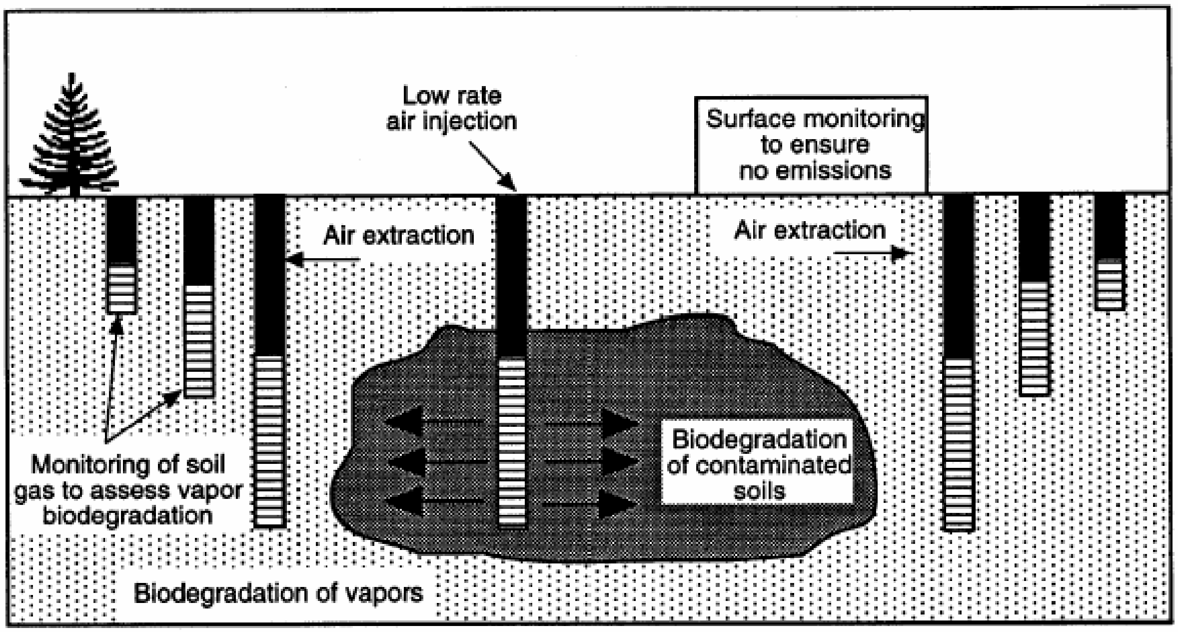


Figure 5: Typical Bioventing Operation (Rockne and Reddy, 2003)

*Limitations*

Due to the complex structure of pesticides, they are not as readily biodegraded as some other compounds (Shanahan, 2004). Further research needs to be conducted to improve current biodegradation methods. Bioremediation of pesticides are also limited by water and oxygen availability, due to the aerobic nature of the discussed methods (Fragoeiro, 2005).

Furthermore, bioremediation has some disadvantages that are important to investigate. In biodegradation, partial degradation which may result in toxic and potentially volatile products is possible (Rockne and Reddy, 2003). As with any process that utilizes the natural environment, all conditions cannot be strictly regulated, and these treatment methods results are variable with differing environmental conditions. To ensure acceptable results, extensive monitoring is required throughout the process (FRTR, 2006). Finally, bioremediation of pesticides requires a longer treatment time than other possible detoxifying processes (Rockne and Reddy, 2003).

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