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# Review

## Fate of Pesticides in the Environment and its Bioremediation

By *M. Gavrilesco\**

The present paper is an overview of the presence and fate of pesticides as persistent organic pollutants in the environment as well as of the potential for their detoxification, also combined with chemical and physical treatment. It contains information gathered from a range of currently available sources. The fate of pesticides in the environment is analyzed considering the processes that determine their persistence and mobility, grouped into transport, transfer and transformation processes. Few pesticide characteristics such as persistence, mobility and biodegradability are emphasized. The fate of a pesticide and the potential for its persistence and mobility from the site of application are considered to be affected by the chemical and physical properties of the pesticide, site characteristics such as soil and groundwater individuality, climate and local weather conditions, biological population, and the handling practices of the pesticide user. Bioremediation, as one of the most environmentally-sound and cost-effective methods for the decontamination and detoxification of a pesticide-contaminated environment is discussed especially considering the factors affecting the biodegradability of pesticides such as biological factors and the characteristics of the chemical compounds. In situ and ex situ bioremediation as possible types of bioremediation activities are weighted up. Also, the paper includes some considerations for developing strategies regarding the choice of bioremediation technology, as well as advantages and disadvantages of the bioremediation of environmental components polluted with pesticides.

### 1 Pesticides as Persistent Organic Pollutants in the Environment

#### 1.1 Considerations Regarding Persistent Organic Pollutants

Persistent Organic Pollutants (POPs) are toxic substances released into the environment through a variety of human activities. They have adverse effects on the health of ecosystems, wildlife, and people.

Different sources such as chemical industry, traffic, combustion of fossil fuels and other organics, water treatment by chlorination and application of pesticides in agricultural areas release organic pollutants into the environment by direct input, transport or precipitation processes [1, 2].

Many of the pollutants of concern are toxic and subsequently were banned when it was discovered that they were hazardous to human health. Unfortunately, in many cases, these compounds are also persistent in nature [3–5]. Long after their use, these chemicals remain in soils and sediments where they can enter the food chain directly or percolate down to the water table. Once in the groundwater, these pollutants can enter drinking water wells and cause health problems. These chemicals are also subject to long-range atmospheric transport. One of the primary concerns is the ability of these chemicals to accumulate within the adipose tissue of

animals. Indirect accumulation or biomagnification in higher trophic level organisms, such as mammals, may cause health problems over time because of the increasing levels of toxic compounds within the body [6–8].

Persistent organic pollutants are organic (carbon-based) compounds that include synthesized substances (e.g., pesticides and PCBs). Other substances are by-products generated as a result of human and natural activity, of which human activity accounts for the major percentage of releases (dioxins and furans). POPs include some of the world's most harmful chemicals including highly toxic pesticides such as DDT, industrial chemicals such as PCBs and unintended by-products of industrial processes and incineration such as dioxins and furans.

Extensive scientific studies have shown that POPs are some of the most dangerous pollutants released into the environment by humans [7, 9, 10]. Contamination of soil, sediments and groundwater by persistent and recalcitrant organic compounds such as chlorinated aromatics, polynuclear aromatics, heterocyclics, and nitroaromatics is a widespread legacy of modern industrial, commercial efforts. The specific locations where chemicals were spilled or released, even decades ago, tend to remain the places having the highest concentrations of these contaminants [11, 12].

Actions to reduce and eliminate production, use and releases of these substances were launched over time [8]. Under this frame, two international legally binding instruments have been negotiated and concluded:

- the Protocol to the Regional UNECE Convention on Long-Range Transboundary Air Pollution (CLRTAP) on

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POPs, opened for signatures in June 1998 and entered into force on 23 October 2003.

- the Global Stockholm Convention on POPs, opened for signatures in May 2001 and entered into force on 17 May 2004.

The Stockholm Convention on Persistent Organic Pollutants considers “that persistent organic pollutants possess toxic properties, resist degradation, bioaccumulate and are transported, through air, water and migratory species, across international boundaries and deposited far from their place of release, where they accumulate in terrestrial and aquatic ecosystems”.

These instruments establish strict international regimes for initial lists of POPs (16 in the UNECE Protocol and 12 in the Stockholm Convention). The Stockholm Convention on Persistent Organic Pollutants focuses on reducing and eliminating releases of 12 POPs (coined the “Dirty Dozen” by the United Nations Environment Program (UNEP)). These 12 chemicals include eight pesticides (aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, mirex, and toxaphene); two industrial chemicals (polychlorinated biphenyls and hexachlorobenzene); and two unintended by-products, dioxins and furans [9, 12].

Both instruments also contain provisions for including additional chemicals into these lists. They lay down the following control measures:

- Prohibition or severe restriction of the production and use of intentionally produced POPs,
- Restrictions on export and import of the intentionally produced POPs (Stockholm Convention),
- Provisions on the safe handling of stockpiles (Stockholm Convention),
- Provisions on the environmentally sound disposal of wastes containing POPs,
- Provisions on the reduction of emissions of unintentionally produced POPs (e.g., dioxins and furans).

The European Community is strongly committed to the effective implementation of these two environmental agreements. It has signed both international instruments on POPs, together with the then 15 Member States. The Community ratified the Protocol on the 30<sup>th</sup> of April 2004 and the Stockholm Convention on the 16<sup>th</sup> of November 2004.

The World Bank is also engaged in ongoing work on Persistent Organic Pollutants (POPs), a new program which aims at working with client countries to protect human health and the environment from POPs throughout the globe [11].

Also, the scientific community works on this problem as a consequence of the fact that hundreds of different chemicals, as pesticides have been developed for use in agricultural and non-agricultural settings.

## 1.2 Short Overview of Pesticide Characteristics

The goal of modern pesticide chemistry is to produce pesticides that are effective in smaller quantities, more target-

specific, and less persistent in the environment. Pesticide structures are developed to mimic, and therefore substitute for specific molecules in targeted biological reactions; i.e., the pesticide mode of action is unique to the targeted pest. Such specificity is achievable with complex chemical structures which disrupt target-specific biological processes to effect the desired control and yield less persistence in the environment.

Pesticides are characterized by their uniqueness of their chemical structure or their patterns of use by the society and their interaction with the environment. They can be classified mainly by considering two criteria: chemical classes, target organism.

Systematic chemical names are rarely short and are not convenient for general use, and so standards bodies assign common names to the active ingredients of pesticides. More than 1000 of these official pesticide names have been assigned by the International Organization for Standardization (ISO), in accordance with an established system of nomenclature ([http://www.hclrss.demon.co.uk/summ\\_groups.html](http://www.hclrss.demon.co.uk/summ_groups.html)).

Fig. 1 illustrates a classification of pesticides on the basis of their significant physicochemical properties and behavior in water and soil [13].

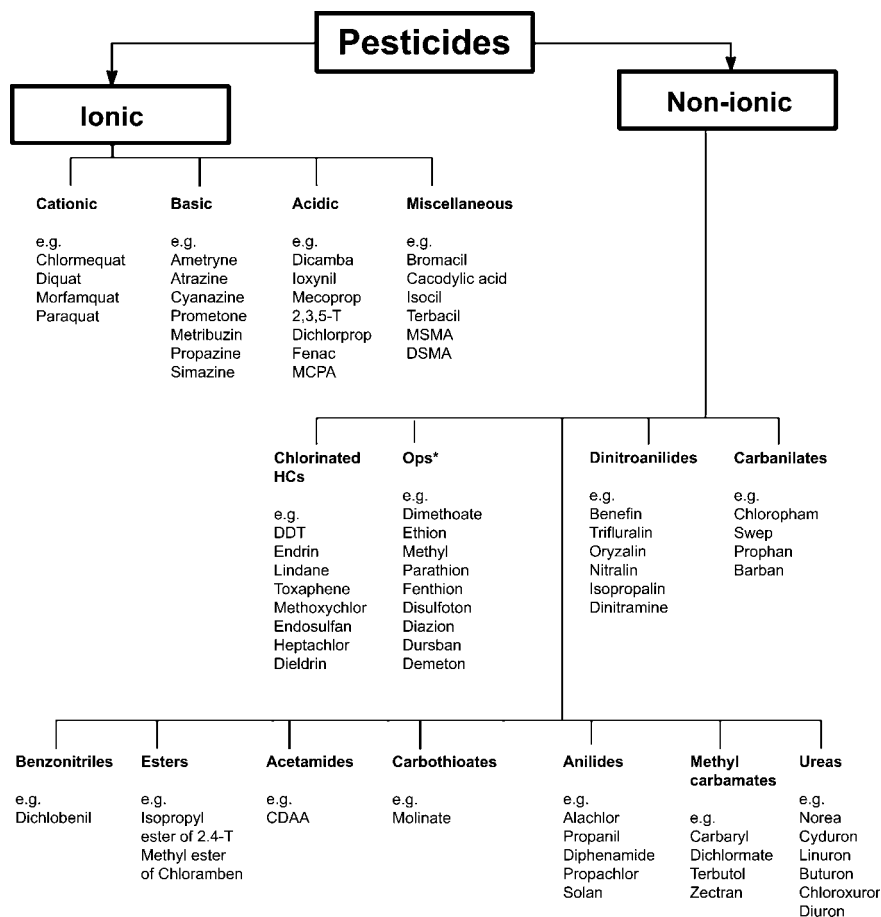
The main types of pesticides are presented in Tab. 1. Chemical structures differ within categories as well as between categories. Individual compounds can occur in more than one group or class, and at more than one place within a group or class. Thus toxicity to humans can vary widely within each group. Each major group of pesticides (e.g., herbicides or plant growth regulators) is subdivided into chemical or other classes (see Tab. 2).

The chemicals applied as pesticides are long-lived, toxic chemicals that can exist for a long time in an ecosystem. The behavior and activity in the environment is clearly dependent on the physicochemical properties of a given pesticide. For instance, organochloride insecticides continue to be detected in surface waters 20 years after their use [10, 12, 14–16].

Therefore, pesticides create hazards in the environment [17, 18]. There are several reasons for not using pesticides [18, 19]:

- Pesticides do not completely solve the pest problems;
- Pesticides are hazardous to human health;
- Pesticides cause special problems for children;
- Pesticides often contaminate food;
- Pesticides are particularly hazardous for farmers and farm workers;
- Pesticides are hazardous to pets;
- Pesticides contaminate water and air;
- Pesticides are hazardous to fish and birds;
- The safety of pesticides and their human health risk were tested by the pesticide manufacturers;
- Pesticides have too many secrets.

There are two main reasons that these compounds persist in nature. First, the conditions necessary for their biodegradation are not ever present. The microorganisms that are ca-



**Figure 1.** Classification of pesticides on the basis of their significant physicochemical properties and behavior in water and soil. (\*Or-gano-Phosphoric pesticides).

**Table 1.** Types of pesticides.

Type	Activity
<i>Algaecides</i>	Control algae in bodies of water, including swimming pools.
<i>Antimicrobials</i>	Kill microorganisms that produce disease.
<i>Attractants</i>	Attract specific pests using natural insect chemicals called pheromones that confuse the mating behavior of insects.
<i>Avicides</i>	Control pest birds.
<i>Biopesticides</i>	Naturally occurring substances with pesticidal properties.
<i>Defoliants</i>	Cause foliage to drop from a plant, typically to aid in the harvesting process.
<i>Desiccants</i>	Aid in the drying process of plants or insects, usually for laboratory purposes.
<i>Fumigants</i>	Produce vapors or gases to control air- or soilborne insects and diseases.
<i>Fungicides</i>	Destroy fungi that infect plants, animals, or people.
<i>Herbicides</i>	Control noxious weeds and other vegetation that are growing or competing with a desired species.
<i>Insect Growth Regulators (IGRs)</i>	Accelerate or retard the rate of growth of insects.
<i>Insecticides</i>	Control or eliminate insects that affect plants, animals, or people.
<i>Miticide (Acaricides)</i>	Kill mites that live on plants, livestock, and people.
<i>Molluscicides</i>	Kill snails and slugs.
<i>Nematicide</i>	Kill nematodes, which are microscopic wormlike organisms that live in the soil and cause damage to food crops.
<i>Ovicides</i>	Control insect eggs through the application of low-sulfur petroleum oils to plants and animals.
<i>Piscicides</i>	Control pest fish.
<i>Plant Growth Regulators (PGRs)</i>	Accelerate or retard the rate of growth of a plant.
<i>Predacides</i>	Control vertebrate pests.
<i>Repellents</i>	Repel pests such as mosquitoes, flies, ticks, and fleas.
<i>Rodenticides</i>	Control mice, rats, and other rodents.

**Table 2.** Classes of pesticides.

Class	Group
<i>Insecticides</i>	Organochlorines Organophosphates Carbamate Esters Pyrethroids Botanical Insecticides
<i>Fungicides</i>	Hexachlorobenzene Organomercurials Pentachlorophenol Phthalimides Dithiocarbamates
<i>Herbicides</i>	Chlorophenoxy compounds Bipyridyl derivatives
<i>Rodenticides</i>	Zinc phosphide Fluoroacetic acid and derivatives $\alpha$ -Naphthyl Thiourea (ANTU) Anticoagulants
<i>Fumigants</i>	Phosphine Ethylene dibromide Dibromochloropropane

pable of biodegrading these toxic compounds may be absent at the contaminated site. If the necessary microorganisms are present, some limiting factors, such as a nutrient shortage, may create unfavorable conditions for the biodegradation of the contaminant. Various cleanup methods, which will be discussed later, have been devised to overcome these limitations in order to make bioremediation more effective [6, 12, 20–22].

The second possibility is that the compound could be resistant to biodegradation. Also, it could be unable to cross the cell membrane for breakdown by intracellular microbial enzymes.

Most persistent pollutants are synthetic, and consequently, the structure of these molecules can be vastly different from naturally occurring structures. If microorganisms have only been exposed to these new and unique molecular formations for the last few decades, then they probably have not had enough time to evolve the mechanisms to detoxify or metabolize them [14].

Whatever the mechanism of persistence may be, these highly stable organic pollutants are widely recognized as a problem.

## 2 Fate of Pesticides in the Environment

### 2.1 Introductory Considerations on the Behavior of Pesticides in the Environment

Pesticide use is an old practice:

*1000 BC:* Chinese used sulfur as a fumigant.

*16th century:* Japanese mixed poor quality whale oil with vinegar for spraying on rice paddies to prevent the development of insect larvae by weakening the cuticle.

*17th century:* Water extracts of tobacco leaves were sprayed on plants to kill insects; *Nux vomica*, the seed of

*Strychnos nuxmomic* (strychnine) was employed to kill rodents.

*19th century:* Insecticides isolated from plants included rotenone from the root of *Derris elliptica* and pyrethrum extracted from flowers of chrysanthemums; Arsenic trioxide was applied as a weed killer; Copper arsenite (Paris Green) was used for the control of Colorado beetle; Bordeaux mixture (copper sulfate, lime, and water) was applied to combat vine downy mildew.

*20th century:* Sulfuric acid (10 %) was used to destroy dicotyledonous weeds without harming monocotyledonous cereal grains and other cultivated plants with waxy coat on leaves.

*1920s:* Public concern because some treated fruits and vegetables were found to contain pesticide residues.

*Post Second World War:* Pesticide development and use increased dramatically in agriculture and public health. Widespread use of pesticides for insect control is to prevent transmission of diseases such as typhus, river blindness, and malaria.

In 1940, 140 tons of pesticides were employed. At that time, the most commonly used pesticides were organics such as plant extracts, and inorganics, which contain heavy metals. During the mid-1940s the production and use of synthetic organic pesticides rapidly increased. By 1991, there were approximately 23 400 pesticide products registered with the US Environmental Protection Agency [23, 24]. In 1997, 600 thousands tones of pesticides were used: the agriculture industry, 77 %; industrial, commercial and government organizations, 12 %; private households, the remaining 11 % [8, 25, 26].

Today, more than 500 different formulations of pesticides are being applied in the environment, and agriculture holds the largest single share of pesticides use. Tab. 2 presents the basic classes of pesticides [27].

Worldwide, research data show that, without effective pest management, pre-harvest crop losses would average about 40 %. Post-harvest activities for pest control must also be compulsory, because without an effective pesticide control, they would create hazards to the environment [28].

It is estimated that four million tons of pesticides are applied to crops annually worldwide for pest control, but less than 1 % of the total applied pesticides gets to the target pests [29, 30].

Their potential as possible carcinogens and their presence in the air, water and soil sources often posed questions about their continuous use in agriculture. Under these conditions, the negative impact of the use of pesticides to human health and the environment have attracted more and more attention [31–33]. The environment is one of the areas where pesticides are considered to present a risk. A number of instruments are available now to control the environmental risk posed by pesticides, including the restriction of chemical use and imposition of taxes [17, 24, 31].

The potential of pesticides to contaminate groundwater or surface water is governed by many factors that include the properties of the soil, the properties of the pesticides, the hydraulic loading on the soil, and crop management practices.

Pesticides vary in the way that they are structured. This is what allows them to “target” certain organisms such as a particular weed or insect.

Variance in chemical structure also helps define how a pesticide will *move* in the environment. Some pesticides are soluble in water, which means that they can move wherever water moves. Some pesticides *volatilize* easily, which means that they can change from a liquid to a gas and move more easily with the air. Other factors to be considered when looking at the chemical structure are based on how they will *degrade* or change their form in the environment and how long it takes for change to occur. During transformation, some pesticides become harmless both to their target organisms and the rest of the environment. Other pesticides may degrade into chemicals that are more toxic than the original chemical. The *daughter* or degradation product(s) may then be toxic to organisms other than the one it was intended for. Pesticides also degrade at different rates in the environment depending upon their chemical structure. For example, soil organisms might degrade a pesticide within days, whereas another pesticide might take hundreds to thousands of years to degrade [34,35]. Degradation or transformation of a pesticide results in a change of structure and will change how it moves in the environment. Transformation may occur in any medium that a pesticide is in.

## 2.2 Processes Involving Pesticides in the Environment

### 2.2.1 Survey on Processes Influencing Pesticide Persistence and Mobility

The fate of pesticides in the environment is influenced by many processes that determine their persistence and mobility. The interaction of pesticides with soils, surface water, and groundwater is complex, being controlled by numerous simultaneous biological, physical, and chemical reactions.

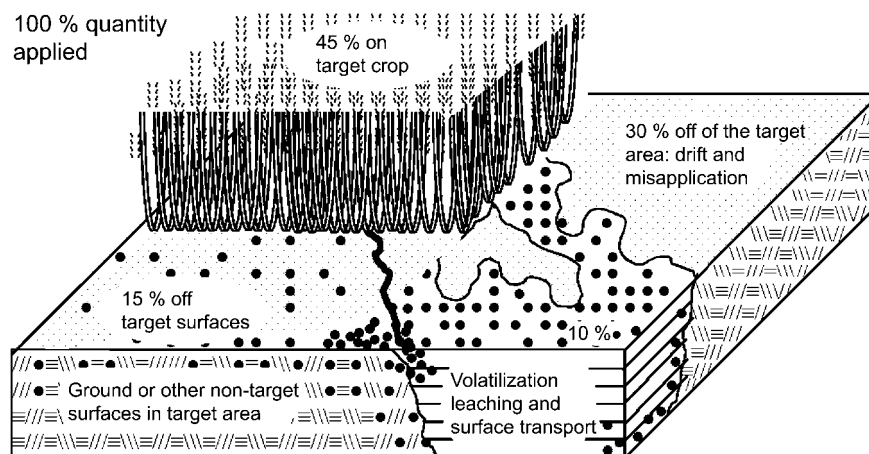
An understanding of the occurrence and distribution of pesticides in bed sediment and aquatic biota requires the consideration of pesticide sources, transport processes, and mechanisms of transformation and the removal from bed sediment and aquatic biota [22,36–40]. In general, the movement of a pesticide from the point of application is controlled first by processes that deliver the pesticide to the stream, and then by processes that deliver the pesticide from the water column to the bed sediment or biota. Once in these places, environmental processes continue to act upon the pesticide. In general, the environmental processes

that govern the behavior and fate of a pesticide in soil as well as surface and ground water can be classified into three types [35, 41, 42]:

- *transport processes*, which move it away from its initial point of introduction to the environment and throughout the surface-water system;
- *transfer processes*, which control its movement among environmental compartments, such as water, biota, suspended sediment, bed sediment, and the atmosphere; transfer refers to the way in which a pesticide is distributed between solids and liquids (e.g., between soil and soil water), or between solids and gases (as between soil and the air it contains);
- *transformation processes* refer to biological and chemical processes that change the structure of a pesticide or completely degrade it. In general, the short-term behavior and long-term fate of a pesticide in surface-water systems are controlled by the physical, chemical, and biological properties of the pesticide (which in turn are determined by its chemical structure) and by the environmental conditions in the hydrologic system.

*Different soil and climatic factors and handling practices* promote or prevent each process (see Fig. 2). The roles of individual soil zone factors [22, 37, 43] can be summarized as:

- Soil texture or the distribution of soil particle sizes influences the rate of water movement through the soil and the active surface area of the soil. Fine textured soils have greater surface area and lower permeability and, therefore, longer contact time and greater sorption area for pollution attenuation. High clay content can be especially advantageous for pollution attenuation because of the very small pore size and the tremendous surface area available for the sorption of cations (positively charged molecules). Some pesticides are inactivated and degraded by sorption to clay colloids. Factors that can alter the effective texture, such as macropore phenomena, should also be considered. This would be



**Figure 2.** Distribution of pesticides on target and non-target areas.

most noticeable in otherwise fine textured soils, such as shrinking clay.

- Soil permeability is the rate of water movement through the soil. This factor is extremely important to the attenuation potential. As noted in the discussion of soil texture, a slow rate of water movement increases the contact time between waterborne pollutants and the soil particles and therefore allows the natural contaminant-removal processes to function more effectively.
- Soil depth influences the amount and time of contact between the pollutants and the soil particles. Deeper soils increase the contact and potential attenuation from inherent physical, chemical, and biological treatment processes.
- Soil pH influences the solubility of pollutants and the rate of biological processes that may remove pollutants. In general, acidic soils tend to increase pollutant solubility, reduce sorption onto soil particles, and reduce the effectiveness of biological treatment processes.
- Soil organic matter influences the sorption potential of the soil and the level of biological activity [44]. Organic matter can bind volatile organic chemicals, metals, nutrients, pesticides, and some pathogens. Organic matter also serves as an energy source for microorganisms essential in the breakdown of organic wastes and pesticides. Wet organic soils may also remove nitrogen through denitrification. Wet organic soils often occur in groundwater discharge areas where pollutants are more of a surface water quality problem.
- Soil slope can influence the amount of water that will infiltrate into a soil. Flat slopes tend to increase the infiltration of water and associated contaminants into the soil and, therefore, the potential local recharge to (and pollution of) the aquifer. Steeper slopes lead to transport of runoff water and associated contaminants to another location down where it either recharges the groundwater or contaminates surface water.

*Pesticide characteristics* are also important in determining the fate of the chemicals in the environment. These characteristics include.

- Solubility in water (water solubility).
- Tendency to adsorb to the soil (soil adsorption).
- Pesticide persistence in the environment (half-life).

Pesticides with high water solubility, low tendency to adsorb to soil particles and long persistence or half-life have the highest potential to move into water. These three factors: soil adsorption, water solubility and persistence, are commonly used to rate pesticides for their potential to leach or move with surface runoff after application.

*Soil adsorption* is measured by the partition coefficient,  $K_{oc}$ , which is the tendency of pesticides to be attached to soil particles [21]. Higher values (greater than 1000) indicate a pesticide that is very strongly attached to soil and is less likely to move unless soil erosion occurs. Lower values (less than 300–500) indicate pesticides that tend to move with water and have the potential to leach or move with surface runoff (see Fig. 3).

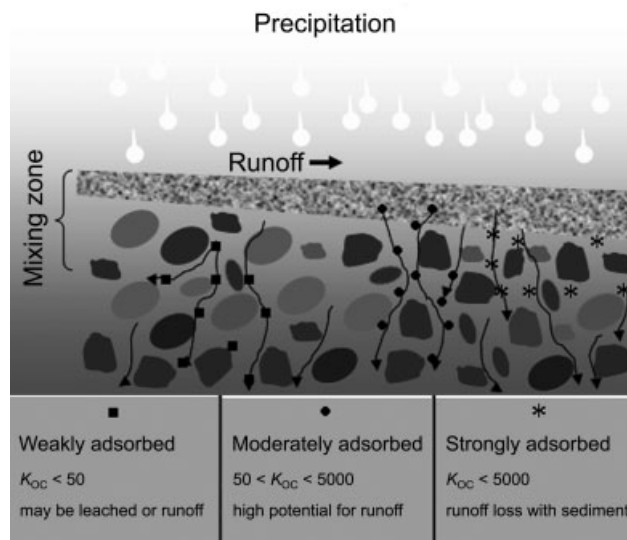


Figure 3. Partition coefficient for pesticide runoff.

*Water solubility* is measured in parts per million (ppm) and measures how easily a pesticide may be washed off the crop, leaches into the soil or moves with surface runoff. Pesticides with solubilities of less than 1 ppm tend to remain on the soil surface. They tend not to be leached, but may move with soil sediment in surface runoff if soil erosion occurs. Pesticides with solubilities greater than 30 ppm are more likely to move with water.

*Pesticide persistence* is measured in terms of the half-life, or the time in days required for a pesticide to degrade in soil to one-half its original amount (see Tab. 3). For example, if a pesticide has a half-life of 15 days, 50 % of the pesticide applied will still be present 15 days after application and half of that amount (25 % of the original) will be present after

Table 3. Pesticide persistence.

Persistence degree	Typical soil half-life
Non-persistent	Less than 30 days
Moderately persistent	30 to 100 days
Persistent pesticides	More than 100 days

30 days. The longer the half-life, the greater the potential for pesticide movement. A pesticide with a half-life greater than 21 days may persist long enough to leach or move with surface runoff before it degrades [34, 35]. Tab. 4 exemplifies the persistence of organochloride pesticides [34].

In this frame, the term *contaminant availability* becomes an important concept; it refers to the rate and extent to which the chemical will be released from the subsurface into the environment and/or is bioavailable to ecological and human receptors. The dissemination of a contaminant after

**Table 4.** Persistence of chlorinated hydrocarbon insecticides in agricultural soils.

Insecticide	Years since treatment	Percent remaining
Aldrin	14	40
Chlordane	14	40
Endrin	14	41
Heptachlor	14	16
Dilan	14	23
Isodrin	14	15
Benzene hexachloride	14	10
Toxaphene	14	45
Dieldrin	15	31
DDT	17	39

its release into the environment is determined by its partition among the water, soil and sediment, and atmospheric phases, and its degradability via biotic and/or abiotic means. These processes determine both the impact and the extent of its dissemination.

No single factor, i.e., adsorption, water solubility, or persistence, can be used to predict pesticide behavior. It is the interaction of these factors and their interaction with the particular soil type and environmental conditions that determines pesticide behavior in the field [16, 46].

Tab. 5 presents the contamination potential with pesticides, as influenced by water, pesticide and soil characteristics [16].

**Table 5.** Summary of groundwater contamination potential as influenced by water, pesticide and soil characteristics.

Risk of Groundwater Contamination		
	Low risk	High risk
Pesticide characteristics		
Water solubility	Low	High
Soil adsorption	High	Low
Persistence	Low	High
Soil characteristics		
Texture	Fine clay	Coarse sand
Organic matter	High	Low
Macropores	Few, small	Many, large
Depth to groundwater	Deep (40 m or more)	Shallow (8 m or less)
Water volume		
Rain/irrigation	Small volumes at infrequent intervals	Large volumes at frequent intervals

(photodegradation, chemical degradation, microbial degradation), and those that affect mobility (sorption, plant uptake, volatilization, wind erosion, runoff, leaching) (see Fig. 5).

The following aspects that should be considered regarding the transport of pesticides need to be clarified:

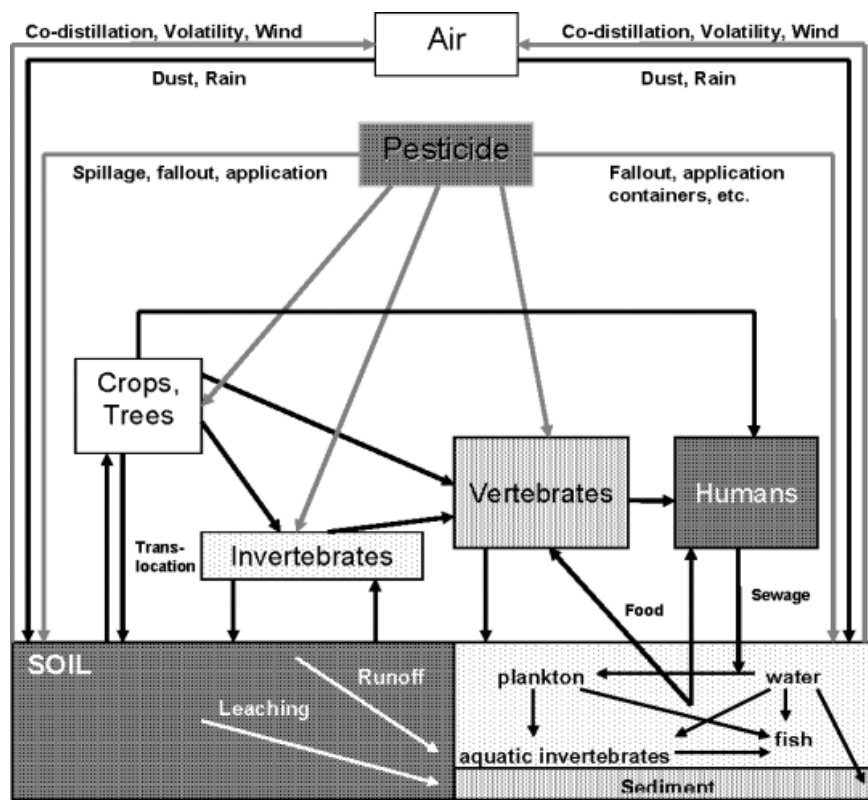
- transport mechanisms;
- proportion of the materials is transported;

### 2.2.2 Transport of Pesticides in the Environment

Pesticides have the potential to move three-dimensionally in many environmental media. The nature of the pesticide and what kind of medium it is transported in will determine the area it will move, the manner it will collect, how fast this will occur, and how long it will reside in the environment. Pesticides can be present anywhere in soil, water, air, and the tissues of organisms (plants, birds, fish, and humans) (see Fig. 4).

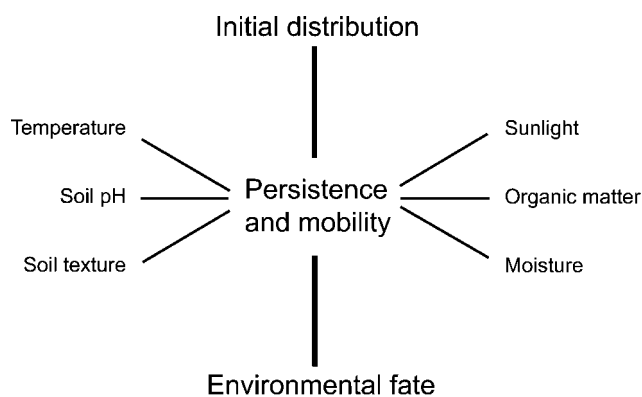
Transportation of pesticides after they are applied to land involves several simultaneous or successive processes, including emission, wash-off, degradation, sorption/desorption, volatilization, leaching, runoff, plant uptake [35, 42, 47].

These processes can be grouped into those that affect persistence



**Figure 4.** Transport of pesticides in the environment.





**Figure 5.** Factors that influence the fate of pesticides in soil.

- fate and behavior of the material during transport;
- biological consequences.

The answer to these questions involves complex treatments of meteorology, aerosol behavior, volatility and solubility of the pesticides, leaching behavior, absorption and absorption properties, photodecomposition, biodegradation, chemical degradation, biomagnification, bioaccumulation, detoxification, effects on non-target organisms, toxicology, etc. This means that environmental dynamics of pesticides could be considered as existing [15, 43, 47].

#### 2.2.2.1 Transport of Pesticides in Air

Pesticides, regardless of the medium that they are applied in, all have the potential to be transported by air. The releasing process of pesticides into the air from agricultural fields – pesticide emission – occurs from plant canopy or soil surface to the atmosphere. The emission strength [20, 21] depends on:

- the vapor pressure,
- the heat of volatilization of the chemical,
- the partition coefficient between the atmosphere and any other phase,
- air flow mass,
- method of pesticide application.

The emission potential of pesticides depends also on the emission factor, generally defined as the ratio of emissions and the usage of pesticide [3, 4, 48–50].

Airborne pesticides can move very long distances and can occur in several ways. They can be carried in the wind during application. Also, they can be transported on small particulates such as soil or on larger objects like leaves that are caught up by wind, and they can volatilize off of any surface that they are applied to. Deposition is what occurs when the wind carrying a pesticide slows down enough that its velocity can no longer hold it in the air, and it falls on whatever is beneath it. This is the so called “dry deposition”. Very small particulates or molecules of pesticide may remain in the atmosphere even when the air is relatively still. These pesti-

cides may be removed from the atmosphere when it rains and the droplets catch them on their way down, through the so called “wet deposition”.

#### 2.2.2.2 Transport of Pesticides in Water

Water transport of pesticides can occur through wet deposition, run-off from surfaces, infiltration of water through the ground, ditches, storm sewers, tile lines, drains, rivers, and open water currents. Water can behave much like air in terms of transporting pesticides. Pesticides can be relatively mobile when suspended in stream or river flow. Transport downstream and dispersion within the reservoirs of the hydrologic cycle result in the potential to affect both human and environmental health over a relatively wide area [14, 47, 51].

Water that is moving at a high velocity can better carry heavier pesticides, or particles that pesticides may be attached to, than water that is moving slowly. Faster moving water also has the potential to move pesticides farther. Pesticides in open water systems may float on the water, diffuse into the water, or deposit onto the sediments at the bottom of the water body. Pesticides that move from the ground surface through the soil may reach shallow ground water or deeper aquifers [52].

Pesticide leaching leads to contamination of subsurface water systems. Due to pesticide loading from surface runoff, erosion, and groundwater discharge to an adjacent river/stream, the related surface water system may also be polluted. The fate of a pesticide and its transport are primarily controlled by subsurface and surface settings as well as agricultural practices, and are influenced by a set of physical, chemical, and biological processes, such as infiltration, evapotranspiration, crop-root uptake, advection, dispersion, sorption, decay, volatilization, etc. [51].

#### 2.2.2.3 Transport of Pesticides in Soils

Once a pesticide is in the soil it will most likely follow one of three pathways [43]:

- moving through the soil with water,
- attaching to soil particles,
- being metabolized by organisms and/or free enzymes in the soil.

Soil texture (percent sand, silt, and clay) and structure plays a great role in the transport processes of pesticides. Soils that are very sandy will allow water to move through them quickly, do not attach easily to pesticides, and generally do not contain a large population of soil organisms relative to other soil types. Soils that are high in clays and organic matter will slow the movement of water, attach easily to many pesticides, and generally have a higher diversity and population of soil organisms that can metabolize the pesticide [21, 26, 36, 37, 53].

#### 2.2.2.4 Transport of Pesticides in Organisms

Generally, pesticides can accumulate in the tissues of organisms. This process (the so-called bioaccumulation) leads to higher concentrations of pesticide [43].

Pesticides that bioaccumulate in organisms are often very persistent in the environment. They do not “break down” easily and retain their form even when ingested and stored in the body. Pesticide-organism interactions are involved in the metabolism, accumulation, and elimination of pesticides by the organism as well as in biodegradation and biological magnification [26, 54]. The movement of a pesticide from the place where it entered an organism to its site of action involves the mobility of the pesticide molecule and the efficiency of the transporting mechanism of the plant or animal, i.e., how quickly the pesticide moves through the plant or animals system. For example, systemic herbicides must move through the plant to areas of interaction [26]. Other herbicides are non-mobile in the plant and only affect the tissue with which they come in direct contact. The extent of penetration depends on the permeability of the organism to the specific pesticide. This permeability differs significantly among plants and insects and even among different tissues of the same organism. Among animals, tissues of the respiratory and digestive system are usually much more permeable than the skin [18, 26]. In recent years there has been much concern about the many pesticides now suspected of being endocrine disrupters, chemicals that can cause effects such as an increase in birth defects and reproductive failure [18].

Most pesticides that have these characteristics have been banned from use, though such pesticides that were used historically are still present in the environment. Banned and restricted pesticides have been eliminated from household products in recent years, but older household pesticides may have been reclassified since the time of purchase. The older the pesticide, the better the chance that it has become restricted or banned, or that it has chemically deteriorated. As a general rule, any pesticide over five years old should not be used until you contact a knowledgeable authority to determine if the pesticide can still be used according to the directions on the label [17, 18, 54]. Different official documents contain lists with banned pesticides. Pesticides Action Network Europe elaborated a document of position signed by 27 governmental and non-governmental bodies, recommending that the precautionary principle apply to the approval of pesticides in Europe when considering endocrine disrupting chemicals (EDCs). Specifically in relation to pesticides approval under Directive 91/414/EEC, PAN Europe recommends, among others, the following [18]:

“1. Pesticides which are publicly agreed on as being endocrine disrupting should be banned according to directive 79/117/EEC. This applies to the pesticides identified by OSPAR in addition to those pesticides classified as being of “high concern” according to the draft EU priority list.

Atrazine, endosulfan and vinclozolin (identified as EDCs by OSPAR) and alachlor, atrazine, fentin-acetate, lindane, linuron, maneb, thiram, vinclozolin, and zineb (classified as being of “high concern” according to the draft EU priority list) should be banned.”

#### 2.2.3 Transfer of Pesticides

Transfer of a pesticide is equivalent to its mobility, being essential for pest control. Usually, a certain pesticide must move within the soil to reach the germinating seeds. Much movement can lead to reduced pest control, contamination of surface and groundwater and injury of other species, including humans.

The ways pesticides can be transferred from one environment component to another are [27, 42]:

- adsorption/desorption,
- volatilization,
- runoff,
- leaching,
- uptake.

##### 2.2.3.1 Adsorption/Desorption

Adsorption on soil is an important physicochemical characteristic governing the fate of pesticides in the environment [55].

The adsorption of pesticides occurs as a result of interactions between a chemical and soil particle.

A pesticide’s tendency to be adsorbed by soil is expressed by its adsorption (partition) coefficient that is the ratio of pesticide concentration in the adsorbed-state (that is, bound to soil particle) and the solution-phase (that is, dissolved in water):

$$K_{OC} = \frac{\text{conc. adsorbed}}{\frac{\text{conc. dissolved}}{\% \text{ organic carbon in soil}}} \quad (1)$$

A common used partition coefficient, which is the ratio of a chemical’s concentration in 1-octanol to its concentration in water at equilibrium in a closed system, is composed of octanol and water [56, 57]. Thus, for a given amount of pesticide applied, the smaller the  $K_{OC}$  value the greater the concentration of pesticide in solution.

High  $K_{OC}$  values indicate a tendency for the chemical to be adsorbed by soil particles rather than remain in the soil solution (see Fig. 3). Since pesticides bond mainly to soil organic carbon, the division by the percentage organic carbon in soil makes the adsorption coefficient a pesticide-specific property, independent of soil type. Adsorption coefficients less than 500 indicate a considerable potential for losses through leaching [58]. This process depends on several factors [15, 58–60]:

#### Soil Characteristics:

- Soil texture: soils rich in organic matter or clay are more adsorptive than coarse, sandy soils because they have more sites onto which pesticides can bind;
- Soil moisture: wet soils tend to adsorb fewer pesticides than dry soils because water molecules compete with the pesticides for binding sites;
- Soil organic matter content: studies have demonstrated that Natural Organic Matters (NOM) enhance the apparent solubility or mobility of highly hydrophobic contaminants (polychlorophenols, PAHs, hexachlorobenzene, some pesticides). On the other hand, the transport of less hydrophobic contaminants was found not to be influenced by NOM;
- pH of the soil;
- Soil particle distribution;
- Temperature.

#### Nature of a Pesticide:

Some pesticides bind very tightly, while others only bind weakly and are readily adsorbed or released back depending on:

- Molecular structure;
- Electrical charge;
- Solubility.

The amount of pesticide sorbed is largely a function of the total amount of organic matter (sorption regions) in the soil. Much organic matter (humus) is made up of a series of organic polymers (long chains or mats of molecules) and generally consists of two systems: a hydrophilic one and a hydrophobic one [36]. No charged or neutral pesticides (nonionic) escape from soil solution into the hydrophobic interior and, as a result, pesticide equilibrium is set up between organic matter and soil solution. In soil, pesticides move between organic matter and water. Also, they may go through an aging process, over time, whereby the chemical travels deeper into organic matter and becomes unavailable to move back into soil solution. Pesticides that are water soluble have a tendency to remain at the surface of soil organic matter, while those that are insoluble will enter to the hydrophobic interior. Sorption to soil particles is also dependent on soil moisture because water is necessary for chemical movement; and water molecules will compete with pesticide molecules for attachment sites on clay and organic matter. Pesticide sorption tends to be greater in dry soils than in wet soils. Decreased soil water content forces the pesticide to interact with soil surfaces. Pesticides that are tightly sorbed to soil particles have decreased mobility and are less likely to contaminate ground water.

Dao and Lavy investigated the effects of soil temperature, moisture content and electrolyte concentration on atrazine adsorption on four soils [61, 62]. Decreasing soil moisture content was found to increase pesticide adsorption regard-

less of soil type. Increasing electrolyte concentrations increased pesticide adsorption. Finally, adsorption decreased as the soil temperature increased.

Wauchope and Myers found that adsorption of atrazine by soil was positively correlated with both the organic matter and the clay content of the soil [62]. The impact of soil particle size distribution on pesticide adsorption has also been examined [62, 63]. Nkedi-Kizza et al. [62] concluded that adsorption of a certain pesticide was stronger on particles smaller than 50  $\mu\text{m}$  than on particles larger than 50  $\mu\text{m}$ . Similarly, Huang et al. found that adsorption of atrazine was stronger on soil particles smaller than 20  $\mu\text{m}$  in diameter [63].

Several models describing the adsorption of pesticides on soil under equilibrium and non-equilibrium conditions have been developed. The most commonly used equilibrium adsorption model is the Freundlich equation. This model has been described by many researchers [61, 65–69]. Bolan and Baskaran examined the adsorption-desorption behavior and the degradation of an ionic herbicide (2,4-D) using 10 soils from New Zealand that differed in their organic matter and clay content [70]. The extent of adsorption, as measured by the distribution coefficient ( $K_{OC}$ ), increased with an increase in soil organic carbon. The rate of desorption of 2,4-D followed first-order reaction kinetics with respect to surface concentration, and decreased with an increase in the organic carbon content of the soils.

Adsorption isotherms of 10 pesticides and their biodegradation intermediates on clay minerals and soils were investigated to predict the fate of pesticides in the environment [71]. The adsorption isotherms were expressed by the Freundlich isotherm equation. Pentachloronitrobenzene, 2,4,6-trichlorophenyl-4'-nitrophenylether, and various intermediates were highly adsorbed on soils, although isoprothiolane was only slightly adsorbed. The adsorbabilities of pesticides on and to soil, gray lowland soil, and montmorillonite were higher than those on allophane and kaolinite.

Disadvantages associated with adsorption of pesticides on soil particles are as follows [15, 55]:

- reduced pest control: for example, if an herbicide is held tightly to soil particle, it cannot be taken by the root of the target weeds.
- plant injury: can result from adsorption of pesticides to soil particles, when a pesticide used for one crop is later released from the soil particles in a greater amount, enough to injure a sensitive rotational crop.

The pesticides may subsequently desorb from soil particles and become surface water contaminants.

#### 2.2.3.2 Volatilization

Volatilization as the process of conversion of solid and liquid pesticide into a gas determines its movement with air currents away from the treated surface [24, 36].

The potential for a pesticide to volatilize, or become a gas, is expressed by its Henry's Law constant:

$$H = \frac{\text{vapor pressure}}{\text{solubility}} \quad (2)$$

A high value for this constant indicates a tendency for the pesticide to volatilize and be lost to the atmosphere. Gaseous losses can be reduced through soil incorporation. Although exchange of soil air with the atmosphere does take place, the rate is so slow that volatilization losses of incorporated pesticides are very low. Pesticides which have volatilized can be redeposited through rain and thereby reach off-target areas. For most pesticides, loss through volatilization is insignificant compared with leaching or surface losses. The main pathway for atmospheric loss of a pesticide is through drift of spray mist under windy conditions, which is relatively independent of a pesticide's chemical characteristics.

The rate of volatilization is dependent on several factors, some of which are similar to those influencing pesticide transport in air:

- temperature: high temperature increases the volatilization;
- humidity: low humidity favors volatilization;
- air movement: is favorable for volatilization;
- soil characteristics:
  - texture: a pesticide tightly adsorbed to soil particles is less likely to volatilize,
  - organic matter content,
  - moisture,
  - pesticide properties,
  - vapor pressure,
  - heat of vaporization,
  - partition coefficient between the atmosphere and other phases,
  - solubility.
- mode of pesticide applications.

### 2.2.3.3 Runoff

Runoff determines the movement of water over a sloping surface that occurs when water is applied faster than it enters the soil. Pesticides carried by surface runoff from agricultural areas are a significant portion of the pesticide pollutant loading rates to surface water bodies. The transport of pesticides in surface runoff depends on the form in which the compounds exist in the water and the hydrodynamics of the system [14]. A pesticide molecule can exist either in the dissolved phase or it can be associated with a particle or colloid. In the dissolved phase, transport of the pesticide will be governed essentially by water flow. In the associated phase, transport will be governed by the movement of the particle or colloid. Pesticides in the associated phase can undergo a variety of transport processes, depending on the type of substrate with which it is associated. Transport of pesticides associated with dissolved organic matter or colloids is also pri-

marily governed by water flow, similar to that of dissolved pesticides. Pesticides associated with particles (sands to clays), or coagulations of very fine particles tend to settle out in lakes and reservoirs, and in low-energy sections of streams, such as backwaters and behind large objects. Because of the tendency of hydrophobic organic pesticides to associate with natural organic matter, they are predisposed to accumulate in bed sediments with relatively high organic matter content (more than 1 %). These sediment deposition areas can serve as long- or short-term sinks for pesticides until the sediments are distributed by the hydrodynamics of the system.

Therefore, the runoff of pesticides depends on [72]:

- the slope of the area,
- soil texture, moisture and erodibility,
- the amount and timing of rainfall and irrigation,
- the presence of vegetation on crop residue,
- physicochemical properties of the pesticide.

Pesticide runoff can lead to groundwater contamination and can cause injury to crops, livestock or humans if contaminated water is used downstream.

In order to reduce pesticide runoff, different practices can be applied, including:

- monitoring of weather conditions,
- careful application of irrigation water,
- enhancing pesticide retention on foliage using a spray mix additive that helps also to better incorporate pesticides into the soil.

The physical processes and spatial variability involved in surface runoff, sediment transport, and dissolved contaminant transport are very complex and are difficult to characterize from a fundamental, conservation-of-mass point of view. Accordingly, the available models all use varying degrees of empirical equations to represent the physical processes. The physical processes are based on the hydrologic cycle. The important mechanisms incorporated, to varying degrees, in different runoff models include precipitation, evapo-transpiration, overland flow, and groundwater recharge/discharge.

A few models also evaluate the transport of dissolved contaminants. The available models for the analysis of pesticide pollution can be generally placed in three categories based on their purposes and formulations: simple pollutant yield models, empirical loading functions, and pesticide transport simulation models [37,39,73-76].

### 2.2.3.4 Leaching

Leaching is the movement of pesticides through the soil rather than over surface. Leaching of pesticides through soil is an environmental concern because of the possibility that they will reach the water table and contaminate the ground water. However, whether a pesticide will reach the groundwater will depend not only upon its movement through the soil, but also upon its disappearance from the soil [77, 78]. If,

for instance, the rate of degradation is sufficiently rapid compared to the rate of leaching, the chemical will disappear before it can reach the groundwater and, therefore, will not pose that environmental problem. The determination of soil leaching rates is important because the rate of leaching of a pesticide indicates how long a pesticide is retained in the top soil where it is most subject to degradation or dissipation [79, 80].

Two kinds of phenomena are associated with leaching [36, 72]:

- Preferential flow that allows pesticide molecules to move rapidly through a section of the soil profile, with reduced likelihood that the molecules will be retained by soil particles or degraded by microbes. Preferential flow is characterized by water that flows rapidly through worm holes, root channels, cracks, and large structural voids in soil.
- Matrix flow that results in a slower migration of water and chemical through the soil structure; the pesticide moves slowly with water into small pores in soil and has more time to contact soil particles.

Factors influencing the leaching rate include:

- Physicochemical properties of pesticides: a pesticide held strongly to soil particles is less likely to leach,
- Adsorption on the soil particles:
  - Solubility: a pesticide that dissolves in water can move better through soil;
  - Persistence: a pesticide that is rapidly degraded is less likely to leach because it may remain in the soil only for a short time.
- Site characteristics:
  - Adsorption capacity (texture, organic matter content),
  - Permeability: the more permeable a soil, the greater the potential for pesticide leaching.
- Method and rate of pesticide application.

Pesticides can reach through the soil to groundwater from storage, mixing equipment, and disposal areas. Leaching through soil is a complex phenomenon with at least four major elements [81, 82]:

- Soil adsorption which determines the underlying pattern;
- Porous flow and diffusion which produce a dispersion of the chemical;
- Adsorption dynamics which introduces a factor of hysteresis;
- Water infiltration and evaporation which determine the actual amount of water movement and, hence, the observed amount of movement of pesticides.

Some results demonstrate that the retarded intraparticle pore diffusion model can predict the desorption rates with a single diffusion rate constant obtained independently from the long-term batch sorption experiment. Also, no evidence for hysteresis was found by Kleineidam et al. [82], considering that many hysteresis phenomena reported earlier are experimental artifacts resulting from non-equilibrium effects and non-physical based models.

The most important factors in determining whether a pesticide will leach are its degradation (persistence) capabilities,

its sorption characteristics, and its preference to release rapidly into soil solution once it is sorbed. Pesticides that are weakly sorbed by soil and resist degradation are more likely to be leached to ground water than are those that remain bound to soil. Pesticides with smaller  $K_{OC}$  values are more likely to be leached compared to those with larger values.

Two different pathways can be used for pesticide leaching through the soil profile: with the water into the soil matrix, and through macropores. Both domains of flow: soil matrix and macropores can move pesticides from the soil surface to deeper soil layers. However, leaching of a pesticide through the soil profile is strongly influenced by preferential flow. Preferential flow is the process in which water and solute rapidly move through soil macropores, bypassing much of the soil matrix. Several factors such as size, geometry, and distribution of macropores affect preferential flow [80].

### 2.2.3.5 Uptake

*Uptake* is the movement of pesticides into plants and animals.

Pesticide uptake depends on:

- environmental conditions,
- physicochemical properties of pesticide,
- physicochemical properties of soil.

The most important factors of influence are the plant species, growth stage, and intended use [83]. Soil characteristics such as the pH, temperature, clay fraction, moisture content, and particularly organic matter content also influence the uptake of pesticides by plants [6, 83]. In addition, the type of pesticide, the pesticide formulation, the method of application, and the mode of action affect uptake [6].

### 2.2.4 Pesticides Transformation

#### 2.2.4.1 Premises

Pesticide transformation or degradation is the major process of loss for most pesticides after their application. Pesticide degradation refers to the breakdown of pesticides within the environment. A pesticide is susceptible to photochemical, chemical, and microbial decomposition [16, 84, 85].

Pesticide degradation or breakdown should change most pesticide residues in the environment into harmless non-toxic compounds. Most are degraded or detoxified by physical, chemical and biological treatments before they are released into the environment. Although the biological treatments are a removal process for some organic compounds, their products of degradation may also be hazardous [86]. Moreover, some non-degradable compounds discharged into the environment along with the treated compounds can cause problems because they usually come back to human beings through several channels such as bioaccumulation.

Tab. 6 presents important physical, chemical, and structural elements that usually determine if an organic compound can be degraded [20].

**Table 6.** Physical, chemical, and structural properties that influence degradability of an organic compound [20].

Property	Degradability	
	More easily	Less easily
Solubility in water	Soluble in water	Insoluble in water
Size	Relatively small	Relatively large
Functional group substitutions	Fewer functional groups	Many functional groups
Compound more oxidized	In reduced environment	In oxidized environment
Compound more reduced	In oxidized environment	In reduced environment
Created	biologically	chemically by man
Aliphatics	Aliphatic up to 10 C-chains Straight chains Aromatic compounds with one or two nuclei	High molecular weight alkanes Branched chains Polyaromatic hydrocarbons
Substitution on aromatic rings	-OH, -COOH, -CHO, -CO -OCH <sub>3</sub> , -CH <sub>3</sub>	-F, -Cl, -NO <sub>2</sub> -CF <sub>3</sub> , -SO <sub>3</sub> H, -NH <sub>2</sub>
Substitutions on organic molecules	Alcohols, aldehydes, acids, esters, amides, amino acids	Alkanes, olefins, ethers, ketones, dicarboxylic acids, nitriles, amines, chloroalkanes
Substitution position	<i>p</i> -Position <i>o</i> - or <i>p</i> -Disubstituted phenols	<i>m</i> - or <i>o</i> -Position <i>m</i> -Disubstituted phenols

Pesticide degradation, as affected by various soil parameters, has been studied by several researchers. Kells et al. [87] and Moreale and van Bladel [88] examined the influence of soil pH on the dissipation of atrazine and 2,4-D, respectively. Kells et al. concluded that degradation rates are lower when soil pH is above 6.5 and higher for soil pH values below 5.0. On the contrary, Moreale and van Bladel reported that 2,4-D losses were greater in soils having a pH above 6.0 than those having a lower pH. In addition, degradation rates were found to be independent of the tillage type and remaining crop residue [87].

Soil temperature, which affects the rates of both microbial growth and death, influences the rate of pesticide degradation. This relationship is expressed in terms of the Arrhenius equation, which holds that the degradation rate always increases with increasing temperature [84, 89, 90].

The effects of soil moisture and temperature on the degradation of carbofuran and 2,4-D have been reported [91, 92]. Both studies show degradation peaks within a soil temperature range from 27 to 35 °C. In addition, Ou et al. [91] found that a soil temperature increase from 15 to 27 °C had a greater impact on carbofuran degradation than did a temperature

increase from 27 to 35 °C. They also found a correlation between the degradation rate and the product of the soil temperature and moisture content for homogeneous data sets. This relation, however, performed poorly when soil-water tension was considered instead of soil moisture content, or when it was used to describe the grouped data. Parker and Doxtader concluded that the rate of decomposition of 2,4-D decreased with increasing soil water tension between soil temperatures of 20 and 35 °C [92]. Also, Zhang et al. examined the kinetics of pesticide degradation at a constant temperature and at fluctuating temperatures [93]. Their analysis revealed that, at the lower and higher end of the temperature growth range, there was a decrease in the growth rate in comparison with that derived from the Arrhenius equation [90].

Degradation is detrimental when a pesticide is destroyed before the pest was controlled. Pesticide degradation occurs by different processes [15, 36, 43, 78, 94, 95]:

- microbial degradation,
- chemical degradation,
- photodegradation.

#### 2.2.4.2 Microbial Degradation

Microbial degradation (biodegradation) is the result of microbial metabolism of pesticides, and is often the main source of pesticide degradation in soils [77, 78, 96]. It occurs when fungi, bacteria, and other microorganisms in the soil use pesticides as a source of carbon and energy, or consume the pesticides along with other sources of food or energy. Researchers have estimated that between 5 000 and 7 000 different bacterial species may exist in a single gram of fertile soil. Populations of bacteria can often exceed one hundred million individuals in one gram of soil, and populations of fungal colonies can exceed ten thousand. The great versatility of microorganisms offers a simpler, inexpensive and more environmentally friendly strategy to reduce environmental pollution than non-biological options [36, 53, 97, 98]. Such biological transformations, which involve enzymes as catalysts, frequently bring about extensive modification in the structure and toxicological properties of pollutants or potential pollutants [20, 21].

Soil organic matter content, moisture, temperature, aeration, and pH all affect microbial degradation. Microbial activity is high in warm, moist soils with neutral pH.

The microbial degradation of pesticides has long been recognized. The exact mechanism for adaptation to pesticides is not entirely understood. Microorganisms may acquire genetic material to encode the biochemical mechanisms necessary to deal with a potential substrate. Recent studies have revealed that microorganism consortia often are involved in the degradation phenomenon [36, 99, 100]. A pesticide in soil solution has to move to these microbial colonies and cross the microbial cell membrane into the cell to metabolize. Some microbes produce enzymes which are exported

from the cell to predigest pesticides that are poorly transported. Once inside an organism, a pesticide can metabolize via internal enzyme systems.

Depending on the specific chemical, the biological degradation may be very fast due to the presence of enzymes; for other compounds the process may be very slow.

The ability of microorganisms to degrade or modify compounds depends on the ability to produce requisite enzymes and ideal environmental conditions for the reactions to occur. In addition, sufficient biomass and communication between the pollutant and the enzymes (intracellular or extracellular) is necessary.

Degradation of organic compounds can be divided into three groups as follows (see Fig. 6) [20].

- Biodegradation starts immediately and the compounds are readily used as sources of energy and growth (immediate degradation);
- Biodegradation starts slowly and requires a period of acclimation before more rapid degradation occurs;
- The compounds are persistent and biodegradation is slow or does not occur.

Various kinetic formulations have been proposed, including first- and second-order forms. It is actually well known that the rate coefficients are functions of temperature, pH, and available nutrients. The second-order kinetics describes the degradation rate as a function of the concentration of the compound and the size of the bacteria population, which is changing as the compound is degraded. A variety of organic compounds may be subject to biodegradation [12, 101, 102].

The biodegradation rate is dependent on an important group of factors such as:

- soil conditions (temperature, aeration, pH, organic matter content),
- frequency of pesticide application (alternating between different classes, groups or formulations of pesticide can minimize the potential for microbial degradation problems as well as pest resistance).

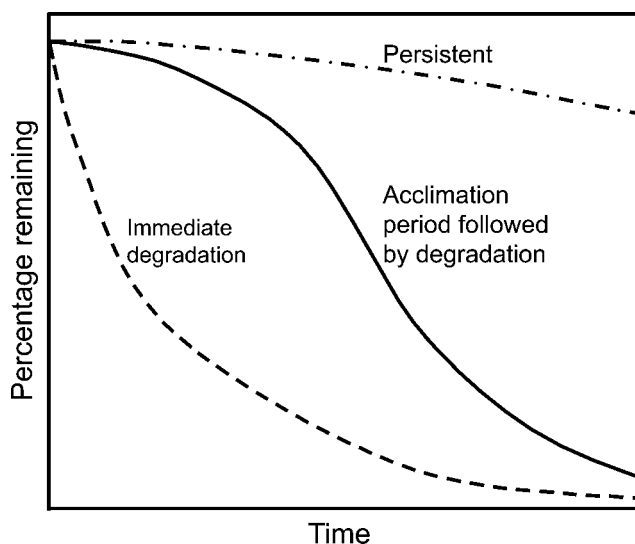


Figure 6. Degradation of organic compounds [20].

### 2.2.4.3 Chemical Degradation

*Chemical degradation* or abiotic degradation occurs by different reactions (including hydrolysis, oxidation-reduction, and ionization that usually happen through the presence of acidity or alkalinity) and is, therefore, related to the pH value [36,43].

#### Hydrolysis

Hydrolysis is the breaking of bonds in a molecule due to reaction with water. Typically a compound is altered in a hydrolytic reaction by the replacement of some chemical groups of a compound with a hydroxyl group. The hydrolysis reactions are commonly catalyzed by the presence of hydrogen or hydroxide ions, and hence the reaction rate is strongly dependent on the pH of the system. Hydrolytic reactions alter the structure of the reacting compound and may change its properties. Depending on the specific reaction, the new compound is usually less toxic than the original compound. Neely listed several functional groups that are susceptible to hydrolytic reactions, including amides, carbamates, carboxylic acid esters, epoxides, lactones, phosphoric acid esters, and sulfonic acid esters [103]. For many functional groups, and therefore a considerable number of compounds, hydrolysis will not occur.

#### Oxidation-Reduction (Redox)

Oxidation-reduction (redox) reactions involve the transfer of electrons from the reduced species to the oxidized species. The oxidation-reduction potential is an important indicator as it allows the oxidation numbers of the metals present in solution to be controlled and the oxidation state and structure of organics to be changed [104].

The redox conditions strongly influence the electron acceptor for microbial activities and thus the biotransformation or biodegradation of chemicals. Examples are as follows ([http://wvlc.uwaterloo.ca/biology447/modules/module8/8\\_main.htm](http://wvlc.uwaterloo.ca/biology447/modules/module8/8_main.htm)):

- oxidation of halogenated solvents by methanotrophs,
- biotransformations with nitrate,
- reductive dehalogenation of halogenated compounds,
- sequential aerobic/anaerobic transformations of halogenated organics,
- chemical reactions mediated by microorganisms.

Oxidation-reduction reactions are used in models in the form of mass action equations with resulting equilibrium constants related to stability. Many redox reactions are very slow, and the concentrations of some species may be far from those predicted via thermodynamic equilibrium. In addition, some redox reactions are catalyzed by metal ions. Some compounds in which redox reactions have been observed to be important include mercury, toxaphene, and

DDT. The rates of reduction reactions are dependent on the pH and the magnitude of the reduction potential. The reduction half-life of the organophosphorus insecticide (OP) parathion, for example, is on the order of minutes in strongly reducing environments [14].

#### *Ionization*

The fate of toxic organics that are either acids or bases can be strongly affected by the concentration of hydrogen ions in a water body. To the same extent, organic chemicals that partition among the gaseous, solid, and solution compartments could be determined from acid-base interactions between the chemical and the aqueous or soil/sediment components of the environment. Since many toxic organics seem to exist in very low concentrations and are at best only weak acids or weak bases, they will have little influence, if any, on the pH values of the water. The hydrogen ion concentration of the water will, however, determine whether acids or bases exist in neutral or ionic forms [105]. An organic acid or base that is extensively ionized could be markedly different from the corresponding neutral molecule in solubility, adsorption, bio-concentration, and toxic characteristics. For example, the ionized species of an organic acid is generally absorbed by sediments to a much lesser degree than the neutral form is. The solubility of an ionic form of an organic chemical will likely be greater than that of the neutral species. Therefore, as a chemical is ionized under environmental conditions, the change in physical properties as well as the chemical reactivity will change with the pH. The pH values found in most aquatic systems range from approximately pH 4 to 9, with extreme values down to pH 2 and up to pH 11 [106].

#### *2.2.4.4 Photodegradation*

Photodegradation is the breakdown of pesticides by light (sunlight) and can occur on foliage, on the surface of the soil, and in the air.

Photochemical degradation (photolysis) occurs whereby radiant energy in the form of photons breaks the chemical bonds of a molecule [106]. *Direct photolysis* involves direct absorption of photons by the molecule. *Indirect photolysis* involves the absorption of energy by a molecule from another molecule that has absorbed the photons. In indirect photolysis, the two steps are usually combined and the photochemical reaction is characterized by first-order kinetics. The reaction rate is dependent on the energy required to break the chemical bonds, available light intensity, and the presence of intermediate compounds making indirect photolysis possible. Characterization of light intensity as a function of depth, time of day, time of year, and dissolved particulate matter in the water column is difficult. These problems add uncertainty to the use of laboratory-derived photolysis rates in field conditions. Mill and Mabey described the types of photolysis reac-

tions affecting a variety of compounds including chloroaromatics, ketones, and aldehydes [107].

All pesticides are susceptible to photodegradation to some degree.

Factors affecting pesticide photodegradation are:

- intensity of sunlight,
- time of exposure,
- properties of the site,
- method of application,
- properties of the pesticide.

Pesticides that are applied to foliage or to the soil surface are more susceptible to photodegradation than pesticides that are incorporated into the soil.

Therefore, the disappearance and fate of a pesticide in soil is dependent upon many factors. These may be summarized as follows:

- *Type of soil*: composition (clay, silt, sand), structure (bulk density, surface area) and prior treatment (chemical and agricultural);
- *Type of the chemical*: physical properties such as solubility, vapor pressure, stability, sensitivity to light, etc., and chemical properties (such as those which affect the adsorption and absorption to organic and inorganic compounds);
- *Climatic conditions*: rainfall, temperature, sunlight, humidity, etc.;
- *Biological populations*: type, nutrient requirements, etc.;
- *Method of application*: granular, solution, suspension, powder, in organic solvents, as wettable powders, etc.

## **3 Removal of Pesticides from the Environment through Bioremediation**

### **3.1 General Aspects Concerning Remediation**

The primary management goal during the remediation of an environmental-contaminated component is to obtain closure, i.e., to achieve a set of conditions that are considered environmentally acceptable and which will ensure that no future action will be required at the site.

Generally, remediation technologies are classified into four categories based on the process acting on the contaminant:

- I. *Removal*: a process that physically removes the contaminant or contaminated medium from the site without the need for separation from the host medium;
- II. *Separation*: a process that removes the contaminant from the host medium (soil or water);
- III. *Destruction*: a process that chemically or biologically destroys or neutralizes the contaminant to produce less toxic compounds;
- IV. *Containment*: a process that impedes or immobilizes the surface and subsurface migration of the contaminant.

*Removal, separation, and destruction* are processes that reduce or remove the contaminant. *Containment* technologies,



on the other hand, control the migration of a contaminant to sensitive receptors without reducing or removing the contaminant. These technologies are used to treat soils, sediments, sludge, solid-matrix waste and groundwater [21, 37].

The research for remedies and techniques for decontamination and detoxification of pesticide-contaminated environmental components is intensive as a result of the impact the pesticide presence in the environment shows [8, 24, 108]. Environmental remediation technologies use physical, chemical, or biological processes that attempt to eliminate, reduce, isolate, or stabilize a contaminant or a group of contaminants [5, 37, 109–112]. Depending on the technology used, the process may either take place at the location of the contamination (in situ), or the contaminated soil or water may be removed for ex situ treatment (see Tab. 7). Every remediation technology has certain limitations and disadvantages. Therefore, site-specific evaluations must be made to assure the appropriate technologies are applied. If multiple contaminants are involved, it may be necessary to use a combination of techniques to reduce the concentrations of pollutants to acceptable levels [37, 111, 113, 114].

Hence, there is an increasing interest in developing safe, convenient, and economically feasible methods for their degradation or transformation. Once in the soil, the pesticide can be removed by technologies based on the following processes:

- Leaching,
- Microbially mediated decomposition,
- Volatilization,
- Plant uptake,
- Nonbiological decomposition.

A summary of several different technologies available for the treatment of pesticide-contaminated sites is shown in Tab. 8 [24].

**Table 7.** Soil remediation technologies.

Method	In situ	Ex situ
Physical	Soil vapor extraction Thermally enhanced soil vapor extraction Containment systems and barriers	Landfilling Incineration Thermal desorption Soil vapor extraction
Chemical	Soil flushing Solidification Stabilization	Soil washing Solidification Stabilization Dehalogenation Solvent extraction Chemical reduction and oxidation
Biological	Bioremediation Phytoremediation	Land farming Bioreactors

The remediation processes by which microorganisms transform or degrade chemicals in the environment are becoming more and more attractive [102, 127].

With advances in biotechnology, bioremediation has become one of the most rapidly developing fields of environmental restoration, utilizing microorganisms to reduce the concentration and toxicity of various chemical pollutants, such as petroleum hydrocarbons, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, phthalate esters, nitroaromatic compounds, industrial solvents, pesticides, and metals [5, 15, 16, 97, 100, 128]. Currently, bioremediation is one of the most environmentally safe and cost-effective methods for decontamination and detoxification of a pesticide-contaminated environment [108, 129]. Nevertheless, bioremediation is a rapidly advancing field and new bio-based remedial technologies are continuing to emerge [15, 16].

The process of bioremediation enhances the rate of the natural microbial degradation of contaminants by supplementing these microorganisms with nutrients, carbon sources or electron donors. This can be done by using indigenous microorganisms or by adding an enriched culture of microorganisms that have specific characteristics that allow them to degrade the desired contaminant at a quicker rate

**Table 8.** Comparison of available technologies for the treatment of sites contaminated by pesticides [24].

Technology	Cost range [m <sup>-3</sup> ] <sup>a)</sup>	Treatment time [month] <sup>b)</sup>	Treatable media <sup>a)</sup>	Removal efficiency <sup>a)</sup>	Source(s)
Low temperature thermal desorption	\$ 70 to \$ 300	0.75	Soil, sludge and sediment	82 % to > 98 %	112, 115
Incineration	\$ 230 to \$ 770	1	Soil, sludge and sediment	Generally > 99.99 %	112
(Off-line) supercritical fluid extraction	No data	(30–120) <sup>c)</sup>	Soil, food, vegetables, humic acid	Up to 99 %	116–120
Bioremediation	\$ 6.4 to \$ 150	3.1 (ex situ)	Soil, sludge, sediment and groundwater	Up to 99.8 %	121–126
Phytoremediation	\$ 60	No data	Soil, sludge, sediment and groundwater	Up to > 80 %	38, 45, 123

a) Based on the treatment of pesticide contaminated media.

b) Based on treatment of 76 m<sup>3</sup> of soil contaminated with various organic compounds.

[56,130]. Bioremediation using microorganisms or biodegradation is the partial or complete conversion of the compound of interest to its elements [5, 24, 131]. Ideally, bioremediation may result in the complete disappearance of the hazardous chemicals [24].

It is usually mediated by microorganisms but many macro-organisms can also biodegrade different compounds, as follows [111, 128]:

- Xenobiotic compounds: those compounds manufactured or used by humans in the course of their activities and thereby introduced as a “foreign” substance into an environment.
- Naturally occurring compounds such as lignin or cellulose – typically, in this case the compounds studied are those that are more resistant to decomposition.

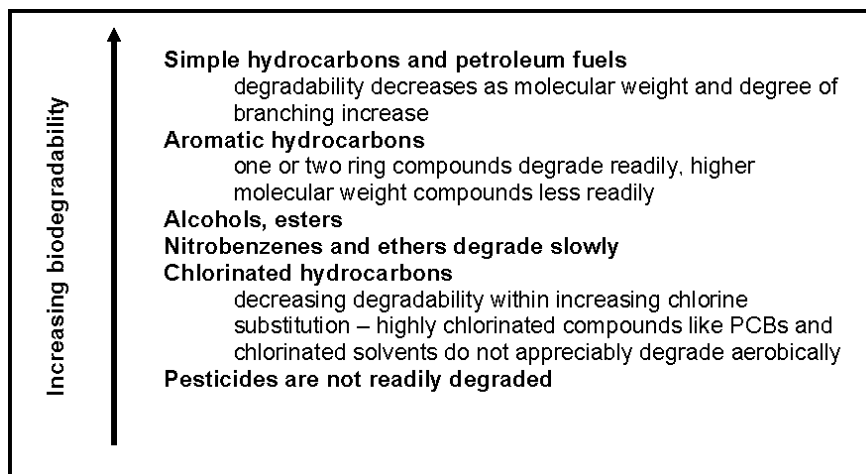
Also, other terms such as “biotransformation”, “partial biodegradation”, and “complete biodegradation” are used to express this process, as well as to distinguish between the complete decomposition of a compound to its elemental form (complete biodegradation) and an intermediate stage of “partial biodegradation” to less complex molecules. “Biotransformation” is also used to indicate the changing of a compound to another reasonably stable molecule, often one that is useful or one that is less or, in some cases, also more toxic than the original. The organisms involved in bioremediation include bacteria, fungi, actinomycetes, protozoa, etc. [15, 95, 128, 132].

The commercial history of bioremediation arises as follows: (<http://ocw.mit.edu/NR/rdonlyres/Civil-and-Environmental-Engineering/1-34Spring2004/335613D5-6D6F-413F-9098-453E8AC20BC2/0/lecture12.pdf>):

- 1972 – first commercial application: Sun Oil pipeline spill in Ambler, Pennsylvania,
- 1970s – continuing bioremediation projects by Richard Raymond of Sun Oil,
- Mid-1980s – emphasis on bioengineering organisms for bioremediation. This technology did not live up to its initial promise,
- 1990s – emphasis switched to greater reliance on natural microorganisms and techniques to enhance their performance.

### 3.2 Biodegradation of Pesticides

The fate of pesticides in the environment is affected by microbial activity. Generally, microorganisms seem to be the most efficient bioremediation agents. Some pesticides are readily degraded by microorganisms, others have proven to



**Figure 7.** Relative biodegradability of organic compounds. (<http://ocw.mit.edu/NR/rdonlyres/Civil-and-Environmental-Engineering/1-34Spring2004/335613D5-6D6F-413F-9098-453E8AC20BC2/0/lecture12.pdf>)

be recalcitrant [77, 78, 85, 95, 125]. They are between organic compounds not easily biodegradable (see Fig. 7) (<http://ocw.mit.edu/NR/rdonlyres/Civil-and-Environmental-Engineering/1-34Spring2004/335613D5-6D6F-413F-9098-453E8AC20BC2/0/lecture12.pdf>). A diverse group of bacteria, including members of the genera *Alcaligenes*, *Flavobacterium*, *Pseudomonas* and *Rhodococcus*, metabolize pesticides. Microbial degradation depends not only on the presence of microbes with the appropriate degradative enzymes, but also on a wide range of environmental parameters [37, 46, 102, 133, 134].

Biodegradation can be categorized into three types that have importance in an ecosystem setting [21]:

- *Primary biodegradation*: biodegradation to the minimum extent necessary to change the identity of the compound,
- *Ultimate biodegradation*: biodegradation to water, carbon dioxide, and inorganic compounds (if elements other than C, H, and O are present) (mineralization),
- *Acceptable biodegradation*: biodegradation to the minimum extent necessary to remove some undesirable property of the compound, such as toxicity (biotransformation).

Microorganisms destroy organic contaminants by using the chemicals for growth and reproduction. Organic chemicals provide carbon, source of cell building material, electrons, and source of energy. There will be different amounts of free energy associated with the various reactions at the different positions (see Tab. 9).

Cells catalyze the oxidation of organic chemicals (electron donors), causing the transfer of electrons from organic chemicals to some electron acceptors [135]. Electron acceptors can be (see Tab. 9) [15, 136]:

- Oxygen, in aerobic oxidation,
- Nitrate, manganese, iron, sulfate (with decreasing efficiency) in anaerobic oxidation.

The organophosphate pesticides, including malathion and parathion appear to be best degraded by aerobic treatment.

**Table 9.** Free energy associated with various reactions at the different positions [15, 136].

Reaction	Electron acceptor	Free energy change
Aerobic respiration	Oxygen	-29.9
Denitrification	Nitrate	-28.4
Manganese(IV) reduction	Manganese(IV)	-23.3
Fe(III) reduction	Fe(III)	-10.1
Sulfate reduction	Sulfate	-5.9
Methanogenesis	Carbon dioxide	-5.6

Groundwater containing organophosphates has been successfully remediated in several pilot and bench studies using aerobic bioreactors. The organochloride pesticides, including chlordane, DDT, and toxaphene appear to require a cycling of the aerobic and anaerobic phase in order to be most successful for remediation. The anaerobic phase reductively dechlorinates these pesticides while the aerobic phase completes the mineralization of the compound [24, 98, 114].

Microorganisms also need essential nutrients such as nitrogen and phosphorus [90, 136, 137].

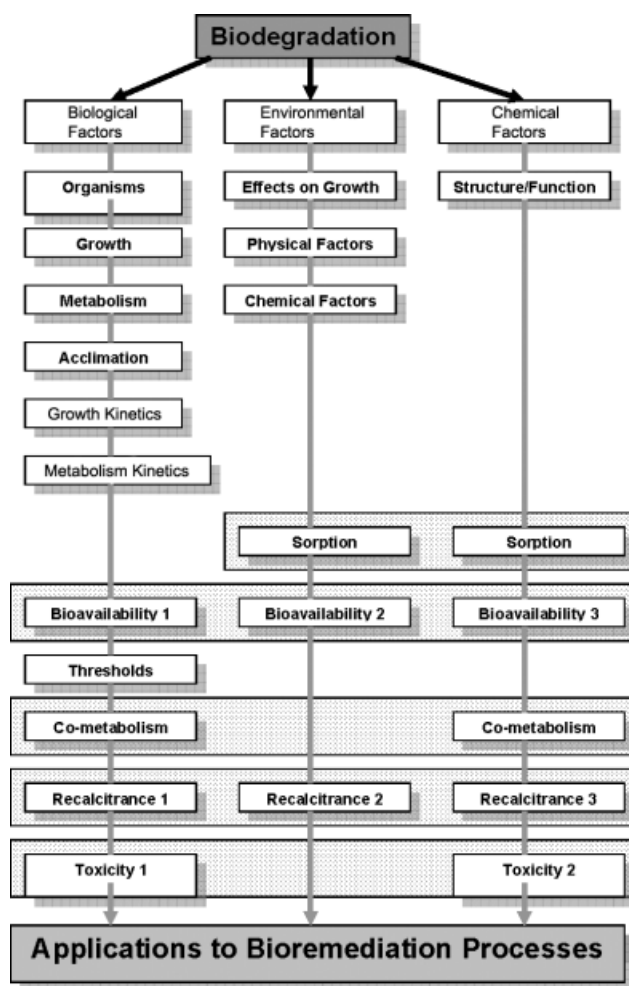
Biodegradation of a given pesticide is a complex process and its results are dependent on the interaction of different factors (see Tab. 10). It is a function of the chemical structure of the compound, the environmental conditions, the organisms and their quantities, the adsorption, release and solubility of the compound, the general bioavailability of the

**Table 10.** Requirements for soil bioremediation.

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	5.5–8.5
Temperature	15–45 °C

compound, and interactions with other compounds present in the environment, kinetics and metabolism, threshold effects, co-metabolic processes, acclimation effects, and others. An overview of factors affecting biodegradation is schematically presented in Fig. 8 and shortly discussed below. The diagram attempts to show the complex series of interacting factors that should be considered in any treatment of biodegradation if it is to be completely understood (<http://wvlc.uwaterloo.ca/biology447/modules/module5/ovbiological.htm>).

Chemical structure and physical/chemical properties have considerable impact on the rate and pathways of biodegradation. The chemical structure determines the possible path-



**Figure 8.** Factors affecting the biodegradation of pesticides.

ways that a substrate may undergo, generally classified as oxidative, reductive, hydrolytic, or conjugative [21, 138]. Fig. 9 provides some examples of common microbial degradation pathways.

Some of these factors are complex interactions of biological, physical and chemical issues. For instance, bioavailability of a compound will depend on these types of interaction. To estimate the possibility of success in a bioremediation project (bottom of the diagram) many of these same factors should be addressed in the planning and test or demonstration phases.

### 3.2.1 Biological Factors Affecting Pesticide Biodegradation

Generally, two biodegradation approaches have been used: one directly based on microorganisms, and the other involving free enzymes [77, 139].

The role of organisms, both micro- and macro-organisms, in pesticide biodegradation is a function of their ecology, biomass characteristics, metabolism (enzyme complement and efficiencies), growth rate, and kinetics (of both growth

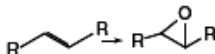
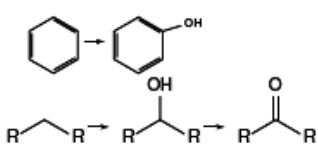
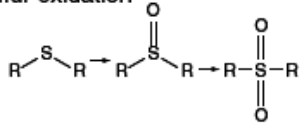
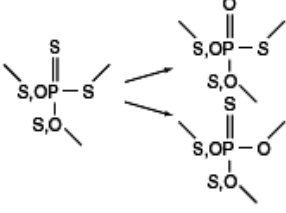
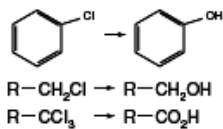
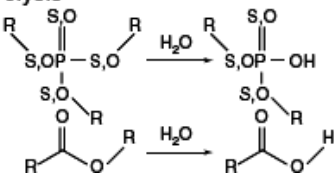
Type of Reactions (not all steps are given)	Example of Chemicals Subject to Reaction
<b><math>\beta</math>-Oxidation</b>	<b>Fatty acids and straight chain hydrocarbons (after oxidation of chain to carboxylic acid - see methyl oxidation)</b>
$\text{CH}_3[\text{CH}_2]_x \text{---} \text{CO}_2\text{H} \longrightarrow \text{CH}_3[\text{CH}_2]_{x-1} \text{---} \text{CO}_2\text{H}$	
<b>Methyl oxidation</b>	<b>Aromatic and aliphatic methyl groups</b>
$\text{R-CH}_3 \rightarrow \text{R-CH}_2\text{OH} \rightarrow \text{R-CHO} \rightarrow \text{R-CO}_2\text{H}$	
<b>Epoxide formation</b>	<b>Olefins</b>
	
<b>Hydroxylation and ketone formation</b>	<b>Aromatic to form phenols and hydrocarbons to alcohols and then ketones</b>
	
<b>Nitrogen oxidation</b>	<b>Aromatic amines to nitroaromatic</b>
$\text{R-NH}_2 \rightarrow \text{R-NHOH} \rightarrow \text{R-N=O} \rightarrow \text{R-NO}_2$	
<b>Nitro reduction</b>	<b>Nitroaromatics aromatic amines (e.g., parathion) especially fast under anaerobic conditions</b>
$\text{R-NO}_2 \rightarrow \text{R-N=O} \rightarrow \text{R-NHOH} \rightarrow \text{R-NH}_2$	<b>Bromoxynil, Dichlobenil</b>
<b>Nitrile/amide metabolism</b>	
$\text{R-CN} \rightarrow \text{R-C(=O)NH}_2 \rightarrow \text{R-CO}_2\text{H}$	
<b>Sulfur oxidation</b>	<b>Sulfides such as aldicarb</b>
	
<b>Thiophosphate ester oxidation</b>	<b>Thiophosphate pesticides</b>
	
<b>Dehalogenation</b>	<b>Aromatic and aliphatic halogens</b>
	
<b>Hydrolysis</b>	<b>Phosphate and carboxylic esters</b>
	

Figure 9. Common microbial degradation pathways [138].

and metabolism) (see Fig. 8). Although most organisms have detoxification abilities (i.e. mineralization, transformation and/or immobilization of pollutants), microorganisms, particularly bacteria, play a crucial role in biogeochemical cycles and in sustainable development of the biosphere [98, 99, 132].

Some biological factors that might not be immediately obvious are [24, 36, 46, 94, 134]:

- The rates of predation of microorganisms by protozoa in the different environments,
- The effects of the rhizosphere (the soil zone around plant roots affected by exudates from the roots) on microbial growth,
- The lytic effects of viruses (bacteriophages) and organisms that excrete enzymes which can destroy the cell walls of other microorganisms.

Microorganisms as a group show a very wide tolerance range for environmental factors (<http://ocw.mit.edu/NR/rdonlyres/Civil-and-Environmental-Engineering/1-34Spring2004/335613D5-6D6F-413F-9098-453E8AC20BC2/0/lecture12.pdf>):

- Very low to very high pH levels,
- A temperature from 0 °C to +80 °C,
- Low to high redox potentials (Eh),
- Low to high nutrient levels,
- Resistance to toxic compounds and elements, etc.,
- Enormous biochemical versatility,
- They are present in very large numbers in most environments – soil contains between 10000 and 100 million microorganisms per gram,
- They can break down the larger insoluble molecules to smaller more soluble sub-units or fragments by means of the hydrolytic enzymes excreted by the microorganisms, as well as smaller molecules (lower molecular weight) that are effectively insoluble.

The mechanisms by which the molecules are transported into the cell where they can be metabolized are as follows:

- A small amount of the pesticide that is soluble in water diffuses through the cell wall – further amounts of the chemical are then only available through further partitioning of the chemical into the water phase,

- Microorganisms secrete compounds (surfactants or emulsifiers) that convert the molecule into very small droplets (much less than 1  $\mu\text{M}$ ) and these are incorporated by the organism in some fashion; the increased surface area due to this emulsification process may be enough in many cases to explain the increased activity simply due to faster partitioning of the compound into the water phase,
- Direct passage through the cell membrane by close contact with the compound (solubilization into the lipid phase of the membranes).

Once the compound is inside the cell, then normal metabolic processes can take place and transform the molecules [36, 99].

Depending on the concentration of the compound, organisms present in the system, and the environmental conditions, the microorganisms exhibit a phenomenon known as *acclimatization* [16, 24, 36, 99] that occurs as a consequence of:

- the growth of initial small populations of microorganisms capable of metabolizing the compound,
- the presence of toxic compounds (including the chemical being examined) that may have to be removed before significant degradation can occur,
- enzyme induction and the *lag* phase.
  - If the compound itself is toxic, then it may then inhibit the faster-growing microorganisms capable of degradation, giving a selective advantage to slower-growing organisms that also degrade it – but initially more slowly until they increase in biomass,
  - Mutation and selection may occur leading to the appearance of new genotypic variations of microorganisms,
  - The microorganisms grow on an easily available substrate before using a less available one (diauxic growth). This might be a factor in systems where only a few different types of bacteria are present.

Bacterial growth kinetics are slightly more complex and follow the classical *Monod-type* kinetics.

In this case, the rate of substrate utilization is proportional to the concentration of the microorganisms present  $[X]$  and is a function of the substrate concentration.

There are a number of compounds in the environment which are transformed by microorganisms, yet it has been difficult or impossible to find organisms that can use them as a source of carbon and/or energy. The compounds may be transformed sequentially by a series of bacteria or other microorganisms, through co-metabolism, because no organisms gained energy sufficient to allow for growth or cell division from the reactions, so that it is necessary to have an alternate or primary substrate for growth under these conditions [140].

### 3.2.2 Characteristics of the Chemical Compounds

Chemical characteristics of pesticides will determine their behavior in the environment and the possibility of bioreme-

diation (see Fig. 8). The main characteristics that influence a chemical compound degradation are [36, 56, 114, 122, 128]:

- Solubility,
- Adsorption,
- Half-life,
- Volatility,
- Bioavailability.

Sometimes, pesticides cannot be biodegraded, although they proved to be biodegradable. Environmental factors (physical, chemical and biological) can have effects on the biological activities of microorganisms (growth rates, kinetics of biodegradation, etc.), sorption of the compound to materials in the environment, toxicity, bioavailability, and the observed recalcitrance of the compounds.

There can be many reasons why a particular pesticide, although biodegradable in testing, is not biodegraded:

#### *The Required Nutrients are Missing*

Often times when specialty compounds such as pesticides, are present in a soil, significant populations of microbes that degrade these compounds are not present. Remediating these soils is generally performed with the aid of bioaugmentation, the development of specific seed cultures and the inoculation of the soil or the bioreactor [85, 114]. For some pesticides such as DDT, Lindane, and heptachlor, anaerobic degradation works better than aerobic degradation [15, 141].

One or more nutrients required for growth are missing. The *limiting nutrient* is the one that is exhausted first in the growth cycle. This assumes that in many cases growth is required for biodegradation; this may not be true if sufficient biomass is already present, or if the compound is degraded by enzymes already present.

#### *The Environmental Conditions are Unsuitable*

There are many environmental conditions that can inhibit growth or metabolism: high or low pH levels, high or low Eh (redox potentials), high temperatures, etc. A good example is in some peat bogs where organic materials may be over 20 000 years old.

#### *The Concentration of Toxic Substances is too High*

Some conditions (high hydrogen sulfide levels, high acid concentrations, etc., may inhibit growth or metabolism).

#### *The Compound May be at a too Low Concentration*

The concentration of the pesticide in the soil also contributes to the rate of degradation. If a compound is degraded through the growth of microorganisms on that compound,

there will be a minimum concentration below which growth will not occur. There will be an even lower concentration that will not even provide maintenance energy levels sufficient for the organism. When the concentration of pesticides present is less than 5 µg/l, then the reaction rate can be described as a first order reaction rate. When concentrations exceed 5 µg/l then the description becomes more complex, and a biphasic breakdown occurs [53].

*The Compound May not be Bioavailable*

Bioavailability can be affected by:

- Sorption to some solid materials in the environment,
- The presence in a non-aqueous phase liquid (NAPL),
- The confinement or entrapment in physical soil or aquifer matrix,
- Complexation.

Many pesticides have hydrophobic properties, so that they tend to bind to suspended particulate matter and accumulate in sediments. Under these conditions, pesticides become less degradable [16, 122, 142]. Also, the hydrophobic properties of these chemical compounds make them accumulate in aquatic biota, which is more hydrophobic than the surrounding water [142, 143].

Ingested particle-associated contaminants may not be bioavailable due to their tight association with particles [36, 144–146].

In sediments, typically between 16–50 % of the contaminants are bioavailable, i.e., available to be taken up and incorporated into living tissue. This is dependent on the characteristics of the compound and sediment, as well as of the biota [147].

In aquatic organisms, the degree of bioconcentration – the accumulation of freely dissolved contaminant in water by aquatic organisms, considering the steady state – can be represented by the bioconcentration factor, BCF, dependent on the rate of absorption and the rate of elimination [35]:

$$BCF = \frac{k_1}{k_2} = \frac{C_A}{C_W} \quad (3)$$

where  $k_1$  denotes the uptake rate constant,  $k_2$  the elimination rate constant for the compound,  $C_A$  the concentration in the organism at steady state, and  $C_W$  the concentration in water at steady state.

The mechanism of bioconcentration from water is comparable to the uptake mechanism of contaminants from pore water. Therefore, this mechanism is also relevant for sediment exposures.

*3.2.3 Bioremediation Processes for Pesticides Degradation*

A number of bioremediation strategies have been developed to treat contaminated wastes and sites polluted with pesticides. Selecting the most appropriate strategy to treat a specific site can be guided by considering three basic principles: the amenability of the pollutant to biological transformation to less toxic products (biochemistry), the accessibility of the contaminant to microorganisms (bioavailability) and the opportunity for optimization of biological activity (bioactivity) [100, 111, 122, 123, 148].

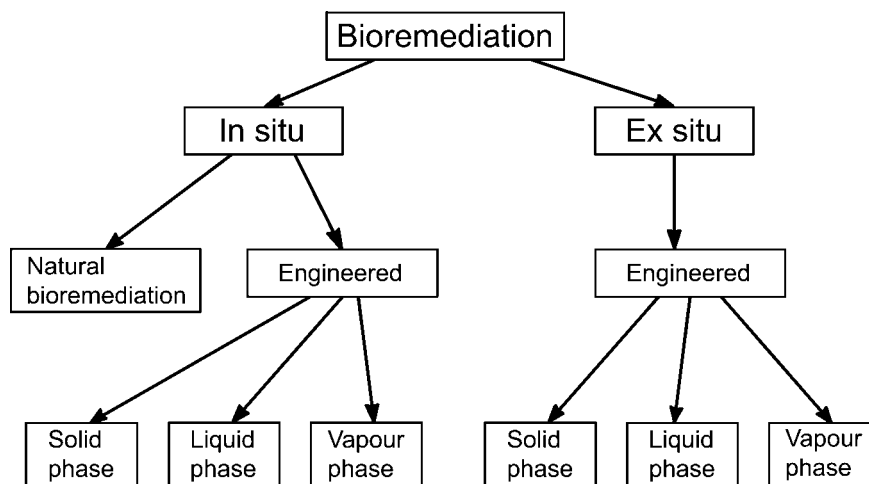
The possible types of bioremediation activities fall into two main categories: ex situ and in situ. In situ bioremediation occurs in the soil, groundwater or other environment without taking away the contaminated material [125, 148, 149]. In contrast, ex situ bioremediation entails the removal of all or part of the contaminated material for treatment (see Fig. 10), ([http://wvlc.uwaterloo.ca/biology447/modules/module8/8c\\_s1.htm](http://wvlc.uwaterloo.ca/biology447/modules/module8/8c_s1.htm)).

*3.2.3.1 In situ Bioremediation*

These techniques are generally the most desirable options due to lower cost and fewer disturbances since they provide the treatment in place avoiding excavation and transport of contaminants [150, 151]. In situ treatment is limited by the depth of the soil that can be effectively treated. In many soils effective oxygen diffusion for desirable rates of bioremediation extend to a range of only a few centimeters to about 30 cm into the soil, although depths of 60 cm and greater have been effectively treated in some cases.

The most important land treatments are [94, 124, 125, 148, 152–154]:

- *In situ biodegradation*: involves delivery of oxygen to the aquifer and may require the addition of other nutrients



**Figure 10.** Classification of bioremediation options.

and/or co-metabolites that are circulated through the contaminated zone to provide mixing and intimate contact between the oxygen, nutrients, contaminant, and microorganisms. Generally, this technique includes conditions such as the infiltration of water-containing nutrients and oxygen or other electron acceptors for groundwater treatment.

- *Bioaugmentation*: involves the addition of microorganisms indigenously or exogenously to the contaminated sites. Two factors limit the use of added microbial cultures in a land treatment unit: i) Nonindigenous cultures rarely compete well enough with an indigenous population to develop and sustain useful population levels and ii) Most soils with long-term exposure to biodegradable waste have indigenous microorganisms that are effective degraders if the land treatment unit is well managed.
- *Bioventing* is a type of biodegradation in which oxygen in the form of air is delivered to contaminated unsaturated soils through a system of extraction and injection wells. It is the most common in situ treatment and involves supplying air and nutrients through wells to contaminated soil to stimulate the indigenous bacteria. Bioventing employs low air flow rates and provides only the amount of oxygen necessary for the biodegradation while minimizing volatilization and release of contaminants to the atmosphere. It can be used where the contamination is deep under the surface, being also a long term cleanup option lasting from several months to years.
- *Biosparging*: involves the injection of air under pressure below the water table to increase groundwater oxygen concentrations and enhance the rate of biological degradation of contaminants by naturally occurring bacteria. Biosparging increases the mixing in the saturated zone and thereby increases the contact between soil and groundwater. The ease and low cost of installing small-diameter air injection points allows for a considerable flexibility in the design and the construction of the system.

The chief benefit of in situ engineering is that it generally involves less surface disturbance than ex situ methods and thereby reduces the potential for human exposure to contaminants. In situ methods also require a minimal amount of facilities [153].

The effectiveness of in situ extraction processes, however, can be limited by heterogeneities in the soil with depth, the presence of silts and clays and uncertainties in flow conditions within the unsaturated zone [154]. In addition, contaminants removed from soil and groundwater via extraction may still require treatment. The use of chemical treatments for in situ treatment often creates unwanted by-products, leaves residues, and can be more toxic or hazardous than the target contaminant [155, 156].

### 3.2.3.2 Ex situ Bioremediation

These techniques involve the excavation or removal of contaminated soil from ground [114, 121, 126, 149, 157, 158].

*Land farming* is a simple technique in which contaminated soil is excavated and spread over a prepared bed and periodically tilled until pollutants are degraded. The goal is to stimulate indigenous biodegradative microorganisms and facilitate their aerobic degradation of contaminants. In general, the practice is limited to the treatment of superficial 10–35 cm of soil. Since land farming has the potential to reduce monitoring and maintenance costs, as well as clean-up liabilities, it has received much attention as a disposal alternative.

*Slurry phase biological treatment* usually consists of a series of large tanks or bioreactor vessels in which water, nutrients, and other additives are mixed with excavated soils or sludges to produce an aqueous slurry. The biodegradation process is carefully controlled in the bioreactor vessel with nutrients, oxygen and pH.

*Composting* is a technique that involves combining contaminated soil with non-hazardous organic amendants such as manure or agricultural wastes. The presence of these organic materials supports the development of a rich microbial population and an elevated temperature characteristic of composting. Composting can be performed using windrows, aerated static piles, or specially designed composting vessels. The contained systems typically allow treatment to be completed in less time than the windrow or aerated pile by providing better control of composting conditions. Rapid treatment time is offset by the high initial cost of the composting reactor.

*Biopiles* are a hybrid of land farming and composting. It is designed to provide optimum temperature, moisture content, aeration, and nutrient conditions to promote rapid biodegradation. In most cases, degradation is achieved by indigenous microorganisms. Essentially, engineered cells are constructed as aerated composted piles [157–159]. Typically used for treatment of surface contamination with petroleum hydrocarbons, they are a refined version of land farming that tend to control physical losses of the contaminants by leaching and volatilization.

*Bioreactors* are ex situ biochemical-processing systems designed to degrade contaminants in pumped groundwater or wastewater using microorganisms. Bioremediation in reactors involves the processing of contaminated solid material (soil, sediment, sludge) or water through an engineered containment system. Bioreactor treatment may be performed using microorganisms growing in suspension in the fluid or attached on a solid growth support medium. In suspended growth systems, such as fluidized beds or sequencing batch reactors, contaminated groundwater is circulated in an aeration basin where a microbial population aerobically degrades organic matter and produces carbon dioxide, water, and biomass. The biomass is settled out in a clarifier, then either recycled back to the aeration basin or disposed of as sludge. In attached growth systems, such as upflow fixed film bioreactors, rotating biological contactors (RBCs), and trickling filters, microorganisms are grown as a biofilm on a solid growth support matrix and water contaminants are degraded

as they diffuse into the biofilm. Support media include solids that have a large surface area for bacterial attachment. The support matrix can be an adsorptive medium, such as activated carbon, that can adsorb contaminants and slowly release them to the microorganisms for degradation, plastic or ceramic packing and even sands and gravel. The microbial population may be derived from natural selection in the reactor, from enrichment from the contaminated media, or from an inoculum of organisms with a specific contaminant-degrading potential.

In general, the rate and extent of biodegradation are greater in a bioreactor system than in situ or in solid-phase systems because the contained environment is more manageable and hence more controllable and predictable [148]. Despite the advantages of reactor systems, there are some disadvantages. The contaminated soil requires pre-treatment (e.g., excavation) or, alternatively, the contaminant can be stripped from the soil via soil washing or physical extraction (e.g., vacuum extraction) before being placed in a bioreactor.

### 3.2.4 Selection of Technologies Exploiting Biodegradation

Bioremediation can be the major type of remediation occurring in a particular technology or it can be a consequence of another technology or an integral part of that technology.

Some elements necessary to be considered to assess remediation technologies are as follows:

- Applicability (target contaminants),
- Minimum achievable concentration,
- Clean-up time required,
- Reliability and maintenance,
- The quality of the decontaminated soil,
- Residuals produced (post treatment needed for by-products),
- Site data needed,
- Overall cost,
- Public acceptability,
- Safety,
- Development status,
- Environmental impacts,
- Performance dependency on site characteristics.

The main groups of technologies employing biodegradation as part or all of their remedial strategies are presented in Fig. 11 ([http://wvlc.uwaterloo.ca/biology447/modules/module8/8c\\_s1.htm](http://wvlc.uwaterloo.ca/biology447/modules/module8/8c_s1.htm)). In addition, factors to be considered during bioremediation planning are highlighted in Fig. 11.

### 3.2.4.1 Enhanced Natural Bioremediation

Natural attenuation known also as intrinsic bioremediation describes the processes that act on a contaminant in the natural environment to reduce contaminant concentrations. These processes may include *dilution, volatilization, biodegradation, adsorption, and chemical reactions*. Although not a technology per se, natural attenuation has been employed at sites where the potential for contaminant migration is low, or where other remedial measures are impractical.

This category includes passive technologies. It relies on the capacity of microorganisms or other organisms in the system to metabolize, remove, reduce, or inactivate the pollutants. It is by definition "in situ". Intrinsic bioremediation or enhanced natural attenuation is an attractive alternative for many sites. The normal microorganisms on the site degrade the toxic compounds without additions, modifications, or interference [160, 161].

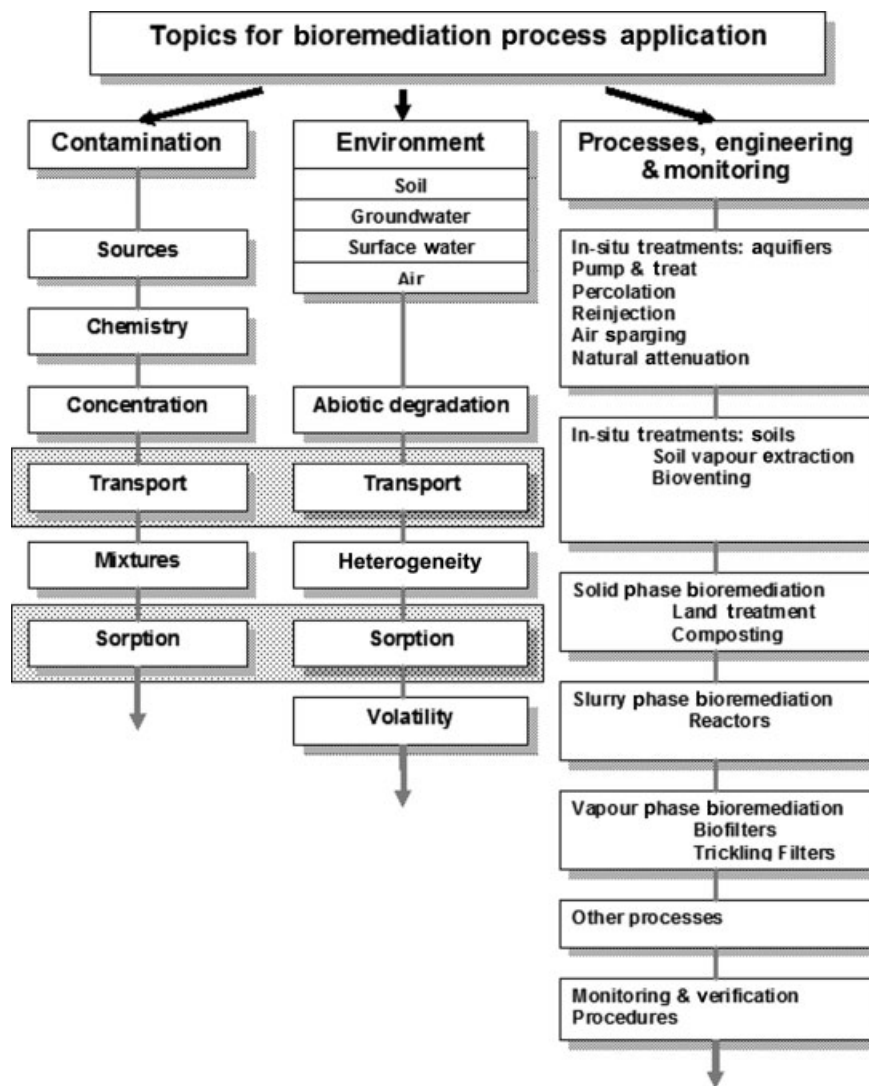


Figure 11. Factors to be considered during bioremediation planning.



Natural attenuation is, or should be, a component of all remedial solutions [20]. Few, if any, remediation technologies can achieve final site-specific remediation objectives like natural attenuation. Therefore, it is important to understand the basics of biochemical reactions, physical attenuation mechanisms, the regulatory basis for the technology, how natural attenuation should be applied, its advantages and disadvantages, and the evaluation process.

Natural attenuation is a “hands-off” remediation approach that relies entirely on natural processes with no human intervention [12, 160]. The natural processes include physical/chemical mechanisms such as dilution, *dispersion* and adsorption of the contaminant [159, 162, 163].

Biological processes, such as the unassisted growth of plants and microbial communities that break down contaminants, can be involved as well.

The primary benefits of natural attenuation are:

- Minimal disturbance of the site, i.e., the site is simply left to be remediated by natural processes,
- Since it involves no human intervention, the operational costs are low to non-existent.

The costs associated with natural attenuation are typically related to monitoring to make sure the process is working.

The main limitation of natural attenuation is that it is slower than any other remediation. In addition, the most appropriate plants and microorganisms may not be present and/or natural environmental conditions may not be optimal to facilitate natural remediation of the contamination. Health risks from the contaminated site may, therefore, exist for a period of time that is not acceptable from either a social or business standpoint [12, 24, 161–163].

### 3.2.4.2 Engineered Bioremediation

Another type is *Engineered Bioremediation* where the operators take an active role in promoting or carrying out the bioremediation process. This can be either *in situ* or *ex situ*. Some processes originally designed to carry out remediation through chemical or physical means are now known to, at least partially, involve bioremediation processes. Typical of these is bioventing where air is passed through a soil or groundwater to volatilize contaminants [94, 125, 148]. It is now thought that the microbial activities in the volume being treated are enhanced by this process.

Many bioremediation examples have used either intrinsic bioremediation or some mechanisms to modify or enhance the activities of these naturally occurring microorganisms. Typically, oxygen or air injection, the addition of nutrients in calculated quantities or the mixing of the system in some way have been preferred choices.

### 3.2.4.3 Decision on Choosing Bioremediation Technology

In order to implement a bioremediation process, a strategy has to be developed that may include ([http://wvlc.uwaterloo.ca/biology447/modules/module8/8c\\_s1.htm](http://wvlc.uwaterloo.ca/biology447/modules/module8/8c_s1.htm)):

- Preliminary site investigation to determine site geochemistry, environmental characteristics, soil conditions, hydrology, hydrogeology, concentration and distribution of contaminants;
- Intrinsic microbial reactions that can and have affected concentration and distribution of contaminants;
- Detailed site investigation to confirm these proposals;
- Using information from the steps above to decide if intrinsic or engineered bioremediation processes could be used to remediate site to required conditions. This is done in relation to the regulations applying to the site and to the proposed use for the site;
- Implement intrinsic or engineered program OR to investigate alternative remediation options;
- Monitor site for the efficacy of the program;
- Modify the program on the basis of on-going analyses and any other developments;
- Terminate the program when “clean-up” goals are reached – completely document the entire process.

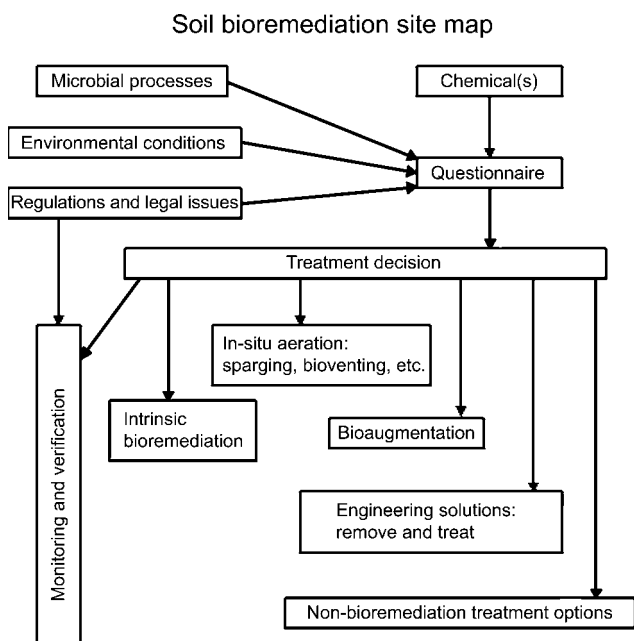
Some decision support tools can be available to facilitate the decision making process [164]. They can be grouped considering at least two criteria:

- The nature of the support:
  - Tools that help to solve the problems involved in decision making,
  - Tools that facilitate knowledge management capabilities,
  - Tools that help to coordinate distributed decision making process,
  - Tools that offer advice, expectations, facts, analyses, etc.,
  - Tools that may play a stimulative role.
- Computer-based decision support purposes:
  - Improve decision making ability of managers (and operating personnel) by allowing more or better decisions within constraints of cognitive, time, and economic limits,
  - Increase productivity of decision makers,
  - Supplement one or more of a decision maker’s abilities,
  - Facilitate one or more of the decision-making phases,
  - Aid decision maker in addressing unstructured or semi-structured decisions.

Fig. 12 shows a rationale and a process to decide on whether or not to try bioremediation to treat contaminated soil as well as questions that should be answered and a series of decision points that can be used to “estimate” the likelihood of bioremediation being successful ([http://wvlc.uwaterloo.ca/biology447/modules/module8/8c\\_s1.htm](http://wvlc.uwaterloo.ca/biology447/modules/module8/8c_s1.htm)). If bioremediation is ruled out as an option, then other non-bioremediation options can be considered. The main reason to try bioremediation first is that it is often the cheapest solution.

Fig. 13 illustrates an algorithm for groundwater bioremediation treatment decision that can facilitate the achievement of information necessary to solve some matters as:

- To identify and systematically compare information about conventional and innovative remediation technologies to meet remediation goals,
- To establish a structured evaluation and selection process,



**Figure 12.** Soil bioremediation scheme. ([http://wvlc.uwaterloo.ca/biology447/modules/module8/8c\\_s1.htm](http://wvlc.uwaterloo.ca/biology447/modules/module8/8c_s1.htm))

- To define consistent and measurable criteria for technology evaluation and selection,
- To provide documented and reproducible evaluation which can be updated as needed information become available,
- To provide a flexible optimized approach for technology evaluation and selection,
- To fasten preliminary steps in feasibility studies,
- To provide a tool for the evaluation of remediation interventions.

The treatment decisions are made in order to answer the following questions ([http://wvlc.uwaterloo.ca/biology447/modules/module8/8c\\_s1.htm](http://wvlc.uwaterloo.ca/biology447/modules/module8/8c_s1.htm)):

- Can the problem site be remediated using intrinsic or natural bioremediation?
- Is an engineered bioremediation solution required (remove and treat, pump and treat groundwater, etc.)?
- What kind of bioremediation method: in situ or ex situ can be applied?
- Can the addition of nutrients (bioaugmentation) or microorganisms improve the cleanup?
- Are non-bioremediation options or a combination required or preferable?

### 3.2.5 Advantages and Disadvantages of Pesticide Degradation through Bioremediation Processes

There is a complex set of interactions between the types and numbers of microorganisms in groundwater, their biodegradative abilities, the groundwater environment and the resulting bioremediation activities. The factors that should

be considered are ([http://wvlc.uwaterloo.ca/biology447/modules/module8/8\\_main.htm](http://wvlc.uwaterloo.ca/biology447/modules/module8/8_main.htm)):

- The geochemical nature of the volume of groundwater,
- The bioenergetics of the process,
- The biotransformation or biodegradation processes,
- Site conditions for bioremediation processes,
- Design, operation and monitoring of the processes.

In addition, there are many factors that affect the selection of potential bioremediation technologies. These include [6, 15, 16, 148]:

- Contaminant type and characteristics (properties, volume, location, exposure risk),
- Site characteristics (soil types, permeability, surface and ground water properties, climate, site infrastructures, topography, location),
- Costs (capital, operating, maintenance),
- Regulatory and public acceptance,
- Remediation schedule.

The dominant factors that may affect the choice of a technology of bioremediation are summarized in the advantages and disadvantages [125, 148–150].

#### 3.2.5.1 Advantages of Bioremediation

Usually, the complete destruction of target pollutants is possible instead of transferring contaminants from one environmental medium to another, for example, from land to water or air. Bioremediation can be applied for the complete destruction of a wide variety of contaminants. Many compounds that are legally considered to be hazardous can be transformed to harmless products. The residues for the treatment are usually harmless products and include carbon dioxide, water, and cell biomass. The benefits of bioremediation include lower costs and less disruption of the contaminated environment when compared to other clean up methods.

Bioremediation can often be carried out on site, often without causing a major disruption of normal activities. This also eliminates the need to transport quantities of waste off site and the potential threats to human health and the environment that can arise during transportation.

Bioremediation is a natural process and is therefore perceived by the public as an acceptable waste treatment process for contaminated material such as soil.

#### 3.2.5.2 Disadvantages of Bioremediation

Bioremediation is limited to those compounds that are biodegradable and requires important site conditions for its success, that include the presence of metabolically capable microbial populations, suitable environmental growth conditions, and appropriate levels of nutrients and contaminants. Contaminants may be present as solids, liquids, and gases. Also, there are some concerns that the products of biodegradation may be more persistent or toxic than the initial com-

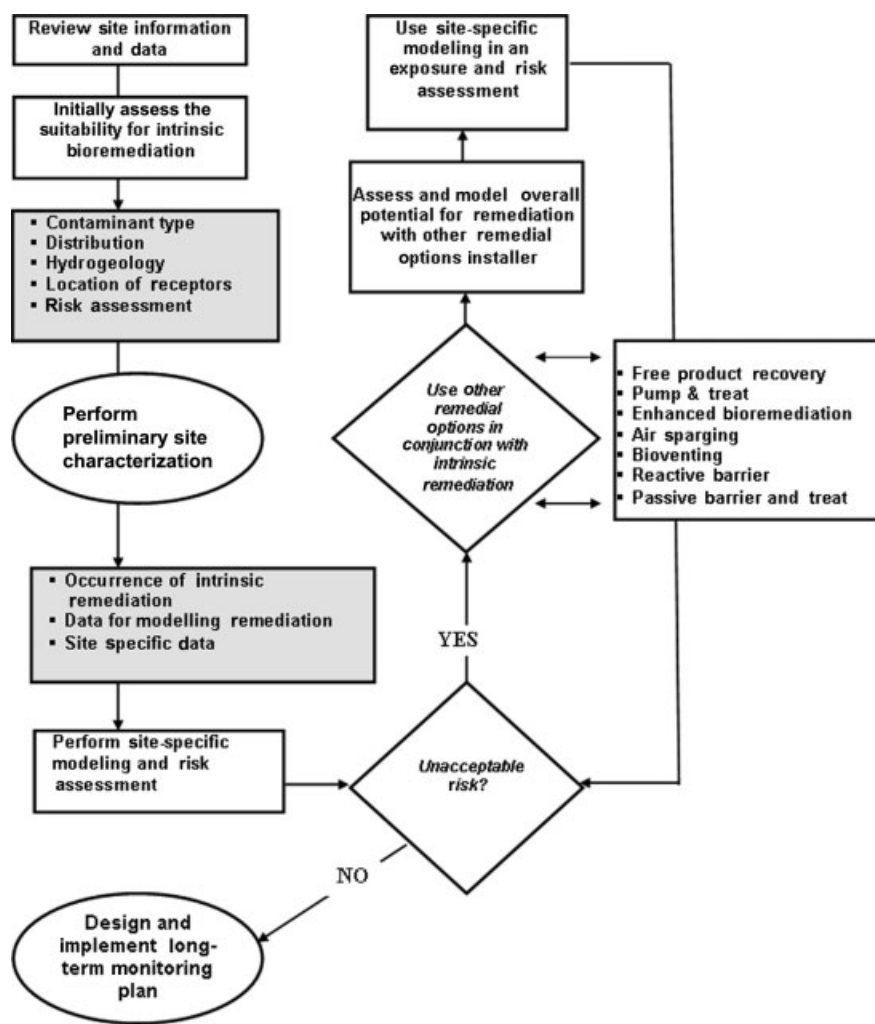


Figure 13. Algorithm for groundwater bioremediation.

pound. Some conditions are necessary to be fulfilled in order to reach adequate bacterial concentrations: electron acceptors, nutrients (e.g., nitrogen and phosphorus), non-toxic con-

ditions (NAPL pools are likely to be toxic), minimum amount of carbon source (which may exceed the regulatory limits for toxic chemicals).

Bioremediation often takes longer than other treatment options, such as excavation and removal of soil or incineration. Also, it is difficult to extrapolate the results from bench and pilot-scale studies to full-scale field operations.

Rapid growth may be limited by diffusive or convective transport of any of the above. Research is needed to develop and engineer bioremediation technologies that are appropriate for sites with complex mixtures of contaminants that are not evenly dispersed in the environment.

The performance of bioremediation is difficult to be evaluated, being often highly specific and there are no acceptable endpoints for bioremediation treatments.

Tab. 11 summarizes some of the advantages and disadvantages of bioremediation [149].

## 4 Conclusions

Pesticides as Persistent Organic Pollutants (POPs) are chemicals which are extremely stable in the environment, bio-accumulate in organ-

isms and food chains, are toxic to humans and animals and have chronic effects such as disruption of reproductive, immune and endocrine systems, as well as being carcinogenic,

Table 11. Summary of bioremediation strategies [22].

Technology	Examples	Benefits	Limitation	Factors to be considered
In situ	In situ bioremediation Biosparging Bioventing Bioaugmentation	Most cost-efficient Noninvasive Relatively passive Natural attenuation processes Treats soil and water	Environmental constraints Extended treatment time Monitoring difficulties	Biodegradative abilities of indigenous microorganism Presence of metals and other inorganics Environmental parameters Biodegradability of pollutants Chemical solubility Distribution of pollutants
Ex situ	Landfarming Composting Biopiles	Cost-efficient Low cost Can be done on site	Space requirements Extended treatment time Need to control abiotic loss Mass transfer problem Bioavailability limitation	See above
	Slurry reactors Aqueous reactors	Rapid degradation kinetics Optimized environmental parameters Enhances mass transfer Effective use of inoculants and surfactants	Soil requires excavation Relatively high cost capital Relatively high operating cost	See above Bioaugmentation Toxicity of amendments Toxic concentrations of contaminants

and are transported in the environment over long distances to places far from the points of release. Pesticides are used widely for increasing agricultural productivity, but more attention should be paid to their potential adverse effects on the environment and human health.

Once a pesticide is introduced into the environment, whether by application, disposal, or a spill, it can be influenced by many processes. These processes determine the ultimate fate of the pesticide by affecting its persistence and movement in the environment. Site characteristics, environmental conditions, crop management systems, and chemical handling practices can all affect each process. The understanding of the fate of the pesticides can help to ensure that applications are not only effective, but also are safe for the environment.

These *fate processes* can have both positive and negative influences on a pesticide effectiveness or its impact on the environment.

Bioremediation provides a technique for cleaning up pollution by enhancing the same biodegradation processes that occur in nature. Bioremediation is an alternative that offers the possibility to destroy or render harmless various pesticides using natural biological activity.

The control and optimization of bioremediation processes is a very complex system. These factors include: the existence of a microbial consortium capable of degrading the pollutants; the availability of contaminants to the microbial population; the environmental factors (type of soil, temperature, pH, the presence of oxygen or other electron acceptors, and nutrients).

Bioremediation can occur either *in situ* (at the site of contamination) or *ex situ* (contaminants are taken away from the site of contamination and treated elsewhere).

Assuming that the site characterization process has shown potentially favorable results from bioremediation as a treatment option, the processes to implement bioremediation activities should be as follows:

- Characterization of hydrological and contaminant site conditions in terms of the microbiological processes;
- Removal of any gross contamination (e.g., leaking tanks or other contaminant source) and any separate immiscible phase (e.g., gasoline pools on surface of groundwater);
- Feasibility studies including sorption studies;
- System design and operation;
- Monitoring system performance.

As such, it uses relatively low-cost, low-technology techniques, which generally have a high public acceptance and can often be carried out on site.

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