

Review. An overview on the environmental behaviour of pesticide residues in soils

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Abstract

The current state of knowledge of the main aspects regarding the behaviour and fate of pesticide residues in the soil environment is reviewed in this article. Once a pesticide is introduced into the environment, whether by application, disposal, or a spill, it can be influenced by many processes. Physical and chemical properties of the pesticide, site characteristics, such as soil, geology, and vegetation, environmental conditions, crop management systems, and chemical handling practices can all affect each process. Each factor must be considered when determining the likelihood of pesticide movement and off-target effect. These fate processes can have both positive (they can bring a pesticide in contact with the target pest) and negative (leading to injury of nontarget plants and animals) influences on a pesticide's effectiveness or its impact on the environment. Processes responsible for accumulation, movement and disappearance of pesticides in the soil and the factors involved in their dynamics are assessed. Also, the environmental significance of the formation of bound residues and some techniques used currently for remediation of pesticide-contaminated soils are discussed according to the recent researches.

Additional key words: accumulation, degradation, movement, persistence, remediation.

Resumen

Revisión. Visión sobre el comportamiento medioambiental de los residuos de plaguicidas en el suelo

Una vez que el plaguicida es incorporado al suelo, bien por aplicación directa, traspaso o accidente, su comportamiento medioambiental se ve influenciado por diversos procesos. Tanto el tipo de suelo y la vegetación presente como las propiedades físico-químicas del plaguicida, las condiciones medioambientales, el sistema de cultivo y/o las técnicas empleadas en el tratamiento fitosanitario pueden influir en cada uno de los procesos, los cuales pueden tener consecuencias positivas (eliminación de plagas nocivas) y negativas (efectos perjudiciales sobre organismos beneficiosos). Por ello, este artículo aborda los principales aspectos relacionados con el comportamiento y destino medioambiental de los residuos de plaguicidas en el suelo, de acuerdo con el estado actual de conocimiento, mediante el estudio de los procesos responsables de su acumulación, movimiento y desaparición y de los factores involucrados en su dinámica. También se examina la importancia medioambiental de la formación de residuos ligados al suelo, y se comentan algunas de las técnicas utilizadas actualmente para la remediación de suelos contaminados por residuos de plaguicidas.

Palabras clave adicionales: acumulación, degradación, movimiento, persistencia, remediación.

Introduction

Of all human activities, agriculture is perhaps the closest to nature. From time immemorial, the farmer has been charged with caring for nature and harvesting her fruits, ensuring the food supply through successive generations. However, the modern day need to boost

production has risen from the need to feed a population that is growing at a vertiginous rate, calculated at 1.8% per year, almost faster than the rate at which food can be supplied. From the approximately 200 million souls living at the outset of the Christian era, the world's population passed 6,000 million at the beginning of the present century. This means a new population equivalent to China's every 12 years (1,300 million), a new European Union (500 million) every 56 months or a new Japan (127 million) every 14 months.

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The responsibility of feeding this ever-increasing population falls to intensive agriculture. However, the negative effects of intensive agriculture on the environment are undeniable. Deforestation, desertification, soil erosion, the exhaustion of arboreal life and genetic resources, salinisation, overexploitation of aquifers, agrochemical wastes are just a few.

Bearing all this in mind, it is clear that humanity finds itself in a very complicated situation and that there might be a temptation to turn a blind eye to environmental concerns; however, at this precise and perhaps opportune moment the concept of sustainable agriculture comes into being, integrating as it does three fundamental objectives: the conservation of natural resources and protection of the environment, economic viability and social justice (Jiménez, 1998). Parr *et al.* (1990) consider that the goals of sustainable agriculture are to preserve natural resources, thereby protecting the environment, attain high productivity and ensure adequate financial returns and improve human health and that of other living things, through the rational management of agricultural systems. Indeed, sustainable agriculture, when practised properly, detains the exhaustion and destruction of natural resources, and foments the sustained and ecologically viable increase in agricultural output; it is, therefore, technically appropriate, economically viable and socially acceptable.

Necessity and problematic of the use of phytosanitary products

The main priority of developing countries is to obtain more and better food, which implies improvements in agriculture through the adoption of different measures, among them the protection of the plants that are being cultivated. In this context, then, that the use of pesticides is important, especially since the green revolution that took place in SE Asia during the 1970's. The chemical fight against agricultural pests has provided, and continues to provide, magnificent service to the farmer. Besides their role in protecting crops and animals, pesticides are also important for the human population and its health. Indeed, one of the first uses of synthetic pesticides such as DDT in the 1940's was in the control of different parasites that attack man or which are vectors of diseases such as paludism, typhus and malaria (Barberá, 1989; Somusandaran and Coats, 1991).

The results obtained in protecting crops and increasing harvests, especially since 1940, meant that synthetic

organic pesticides have become so widely used that other methods of control have been reduced to a complementary role. In other words, it is obvious that if the use of pesticides is reduced, it would be impossible to feed the world's growing population. Although losses due to pests continue to fall, losses still occur but, what is clear is that without pesticides they would be much greater and the price of raw materials, and especially transformed foods, would increase tremendously. However, since all forms of life are interconnected, it must not be forgotten that such compounds can also provoke undesirable toxic effects in some cases. Accordingly, the last three decades have seen a notable improvement in the methods capable of defining the environmental impact of pesticides and the goals of environmental conservation have become clearer. Much has been learnt about the derived problems of an incorrect use. The methods used to study their environmental fate have improved enormously and much has been learnt about the behaviour of pesticides in different media (Koester and Moulik, 2005).

It should be mentioned that the dynamics of these compounds has been widely studied in plants and animals in an attempt to control residues in the food we eat. However, in the last 30 years, research has largely turned to investigating their behaviour in soil because of the strong interaction that phytosanitary products undergo in this medium. Unlike in humans and/or water and the atmosphere, pesticides tend to remain longer in the soil, where they are generally metabolised or diluted more slowly.

It is clear, then, that the occurrence of toxic residues in the soil is an important problem and must be given due attention, as attested by the large number of studies dedicated to this theme in recent years (Barriuso *et al.*, 1997; Hernández *et al.*, 1998; García-Valcarcel and Tadeo, 1999; Reichman *et al.*, 2000; Sheng *et al.*, 2001; Frank *et al.*, 2002; Graebing *et al.*, 2003; Beulke *et al.*, 2004; Barraclough *et al.*, 2005; Rodriguez-Cruz *et al.*, 2006). Despite this, public concern about the possible adverse effects caused by pesticides in the environment has not diminished. Indeed, this concern may well have been fed by the numerous publications and articles directed at the general public, which describe, sometimes based on scientific research but frequently not, the ecological damage produced by the agricultural use of pesticides. This is not to deny that rapid progress in phytosanitary technology led to the possible negative effects on the environment being overlooked for many years and also to the abandonment of agricultural prac-

tices that had for generations served to maintain the biological balance between pests and crops.

Both these errors have now been largely rectified, although «chemiphobia» still tends to exaggerate the risk of using phytosanitary products and overlook the real benefits that they have brought. However, such benefits are much less eye-catching to the popular press, of course. On the other hand, it is not to be denied that residual levels of such products may represent an important source of contamination, especially after prolonged use. Their mobility in the atmosphere and water, their accumulation and/or transformation in the environment and finally their biomagnification really do constitute a risk for human health, wild life and the environment, although we should never lose sight of the benefits they have brought as regards increased yields and better quality foods, etc.

Environmental behaviour of xenobiotics

The physical, chemical and biological conditions that surround an organism constitute its environment. The physical medium is constituted by four constituents: the atmosphere (air), the hydrosphere (water), the lithosphere (soil) and the biosphere (living organisms). The atmosphere is mainly gaseous; natural waters constitute the liquid phase above 0°C; the soil is a solid mixture of clay, silt, sand and organic matter; and lipids are a fundamental component of living organisms. However, these phases are rarely homogeneous, and the soil is really made up of water, air, minerals and organisms, while air contains liquid water in the form of rain and solid particles, etc.

Accumulation of environmentally persistent chemical pollutants is increasing societal concerns about environmental sustainability and the health of ecosystems and humans. These contaminants originate from human activities, such as combustion related to energy production, industrial processes, and agriculture, and accumulate in various environmental compartments. Although xenobiotics (chemical substances unrelated with nature and found in the environment (e.g. pesticides, medicaments, industrial wastes, etc.) are deposited in a given compartment of the environment, they, more or less, rapidly tend to pass to (an) other adjacent compartment(s), as shown in Figure 1.

Many of these chemicals share physical-chemical properties. They are semivolatile organic compounds

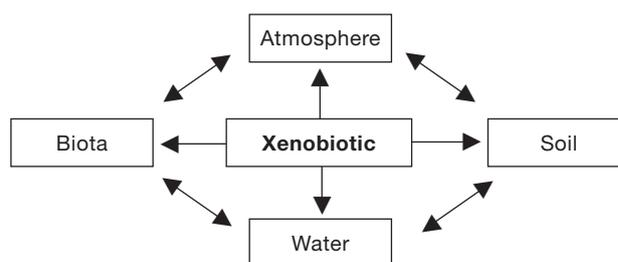


Figure 1. Compartmental distribution of xenobiotics in the environment.

(SVOCs) with vapour pressures typically between about 10^{-1} and 10^{-5} Pa; they are resistant to degradation, and they are lipophilic, partitioning into carbon and liquid phases of the biosphere. As a result, many of these compounds can persist for years, and thus have labelled as persistent organic pollutants (POPs).

Fugacity (the tendency of a compound to pass from one phase to another) is the process responsible for the distribution of a xenobiotic among different environmental compartments. Theoretically, a xenobiotic will escape from its initial compartment to reach an equilibrium concentration with one or more others (Smith *et al.*, 1988; Schwarzenbach *et al.*, 2002). Although such an equilibrium is rarely reached, its theoretical behaviour is an important tool for predicting its distribution in the environment, which will take place between a solid, gas or liquid and a liquid (solution), a solid or liquid and a gas (volatilisation), a solution and a solid surface (adsorption) or a solution and an immiscible liquid (distribution between liquids and bioconcentration).

Ecological effects of pesticides

Interest in the ecological effects of xenobiotics began to be aroused in the 1950's and 60's, when the consequences of using certain pesticides began to be noticed in wild flora and fauna. Thus, in her book «Silent Spring» published in 1962, Rachel Carson drew attention to the danger of DDT and other organochlorine insecticides accumulating in living things. The polemic associated with these chemicals is clear today. Most of them are synthetic chemical compounds deliberately prepared to be toxic towards certain organisms. But since there is certain homogeneity between all forms of life, their accidental consumption by those forms for which they were not intended may well provoke undesirable effects. A handsome anniversary edition of the classic environmental study was recently published (Carson, 2002).

There is a large number of pesticides currently in use, with a wide range of physico-chemical properties and belonging to a wide variety of chemical classes. Pesticides can be classified in many different ways: according to the target pest, the chemical structure of the compound use, the action mode, or the degree or type of health hazard involved.

The unwanted effects caused by pesticides may be grouped into four categories (Navarro and Barba, 1996): i) carelessness and accidents, for example, fish killed by accidental spills or the uncontrolled washing associated with treatment tanks and equipment, ii) alteration of wildlife, following the erroneous use of a pesticide, as occurred in some rice crops or seed treatments, iii) damage caused by pesticide residues, such as liposoluble capable of slowly degrading and accumulating in the fatty tissues of organisms, or the water-soluble contaminants of groundwater systems, and iv) indirect effects as a consequence of the alteration of the environment by phytosanitary treatment, for example, the elimination of aquatic weeds and consequent deoxygenation of the water and resulting threat to fish life, or the terrestrial equivalent of eliminating weeds only to see the wildlife severely affected.

The potential risk involved when a pesticide is incorporated in the environment depends on many factors: the toxic properties of the compound, the amount applied, the type of formulation, method and time of application and, especially, its mobility and persistence. Certain effects of pesticides on wildlife are frequently too complex to be reproduced in the laboratory or field because of the great diversity of practical conditions in which pesticides are used. However, in many cases the probable effects of a chemical compound in the environment can be prevented from an understanding of research results.

Studies to be carried out must take into consideration the characteristics of the product in question and the foreseen conditions of use. Among the basic things needed to know to avoid environmental damage are the following: i) the identity of the active ingredient, ii) the physico-chemical properties of the active ingredient will govern its behaviour in the soil and its biological activity iii) the composition of the toxic product, and iv) the formulation of the product. All these factors are of great importance for predicting the behaviour of the product in the environment, although other properties, too, must be taken into account, among them: molecular size, ionisability, water solubility, lipophilicity, polarisability and volatility are all key

properties, but generally one or two properties have a dominating influence.

Researches aimed at understanding the behaviour and mobility of a pesticide in a given medium are based on analytical methods capable of determining residual concentrations in different media, degradation and concentration rates of the wastes present in plants, soils and waters, identity of the principal metabolites in some of the above media, and leaching in soil. It must be remembered that the data obtained concerning the toxicity of a pesticide will be of great use for evaluating the possible risks for human beings, the end-users of agricultural production. The principal parameters to be studied in this respect will be acute, semi-chronic and chronic toxicity and the results of metabolic, teratogenic studies, etc. Finally, the way in which a pesticide is used greatly influences its effects on the environment. Very toxic compounds may even have not harmful effects on the environment, if they are applied in a way that they cause no damage to the organisms against which they are directed. Similarly, products of low toxicity and persistency may have harmful effects if they are applied in high doses or very frequently.

The *type of formulation* has a great influence on the persistence and bioavailability of pesticides. For example, granules normally increase the persistence of a compound, although this form may limit attendant biological effects. The *way of application* also has an effect. The effect of an ultra-low volume, for example, will not be the same as for a high volume, or a terrestrial treatment the same as an aerial treatment. The *site of treatment* is also important. Local treatments create fewer environmental problems than extensive treatments. The *time of application*: to eliminate certain pests it may be necessary to apply pesticides at a time which is dangerous for beneficial species, for example, bees. The *dose* has a decisive influence. Frequent and extensive applications may give rise to resistance phenomena. Finally, *climate* and *geographical position* obviously play a part. The results obtained in a given area of the world are not necessarily extrapolable to areas with different climatic characteristics. Solar radiation may favour photodecomposition and the conversion of the original product into one or more of greater or lesser toxicity. It should also be remembered that the toxicity of certain pesticides for aquatic organisms varies with temperature.

All the above factors must be taken into account when evaluating the possible environmental impact and where to locate deposits, which will make it possi-

ble to estimate the degree of exposure of certain species to a given pesticide.

Dynamics of pesticides in the soil. Processes and factors involved

The excessive and uncontrolled use of phytosanitary products in agriculture has occasionally led to severe environmental contamination and degradation. In general terms, the elements of the medium most directly affected by these treatments are water, the soil, fauna, flora and last, but not least, man.

The ideas that reigned during most of the last century, at least until the seventies, concerning the earth's capacity for self-depuration through the dilution of contaminants in the soil, water or air are no longer tenable. We now know that Nature has certain mechanisms for keeping such contaminants and concentrating them, behaviour that can provoke not only serious alterations in the ecological balance but also undesirable toxic effects in the forms of life affected.

The presence of pesticides in agricultural soils may have a variety of origins. They may come, for example, from treatments applied to the aerial part of crops to combat pests, when approximately 50% of the product may reach the soil. Such is the case with many insecticides and fungicides, and some herbicides. Other times, as with nematicides, disinfectants and mainly herbicides (triazines, dinitroanilines, etc.), the soil itself is treated, which will obviously lead to higher concentration in the same.

Persistence

Persistence may be defined as the tendency of a given compound, a pesticide in this case, to conserve its molecular integrity and chemical, physical and functional characteristics in a medium through which it is transported and distributed after being released into the environment. Many organic compounds persist for long periods in soils, subsoils, aquifers, surface waters, and aquatic sediment. The low- and high-molecular weight compounds that resist biodegradation are known as recalcitrant molecules. Many pesticides, mainly herbicides, have this characteristic.

From an agronomic point of view, it is a desirable characteristic that pesticides persist a sufficient length of time to control pests throughout the cultivation cycle.

However, from an environmental point of view, molecules that persist in nature are undesirable for many reasons. Some are intrinsically toxic and deleteriously affect human, domesticated animals, agricultural crops, wildlife, fish and other aquatic organisms, or microorganisms. The longer the molecule remains in nature, the greater is the exposure of susceptible individuals or populations and the greater is the risk or harmful effects (Alexander, 1994). Some recalcitrant pesticides are not toxic at the concentrations found in the environment, but they reach hazardous levels because they are biomagnified in natural food chains. Therefore, it is important to know the process by which a substance is degraded in order to determine whether it will accumulate in the soil or organisms or pass into ground waters and whether it will persist in either.

Once incorporated in a soil, a pesticide enters a dynamic ecosystem in which it will begin to move, degrade *in situ*, move from the initial system to other systems or remain in place with its original structure intact or degraded to a greater or lesser degree for a variable length of time. The pesticide disappears from the soil in three steps. Prior to the degradation of many pesticides, a period is noted in which no disappearance on the compound is evident. This time is known as *acclimation phase* or, sometimes, as adaptation or lag period (length of time between the addition or entry of the pesticide into the soil and evidence of its detectable loss). During this interval, no change in concentration is noted but then the disappearance becomes evident and the rate of loss often becomes quickly (*dissipation phase*). Finally, the last period is the *persistence phase*, which is longer, and is expressed in units of time: hours, days, weeks, months and even years. The term usually used to express persistence is half life time ($t_{1/2}$), which is defined as the time necessary for half the quantity of pesticide originally present or deposited in the soil to dissipate. In certain cases, some authors consider the term «disappearance time» to be more correct (expressed as DT_{50} , DT_{75} and/or DT_{90}), which indicate the time necessary for 50, 75 or 90% of the initial concentration to disappear.

The soil-pesticide-plant interaction is quite complex (Fig. 2). In the dynamics (inactivation, losses and transformations) several processes of a physical, chemical and microbiological type intervene, all related and responsible for the dynamics. Adsorption is probably the most important mode of interaction between soil and pesticides and controls the concentration of the latter in the soil-liquid phase (Navarro *et al.*, 1992; Navarro

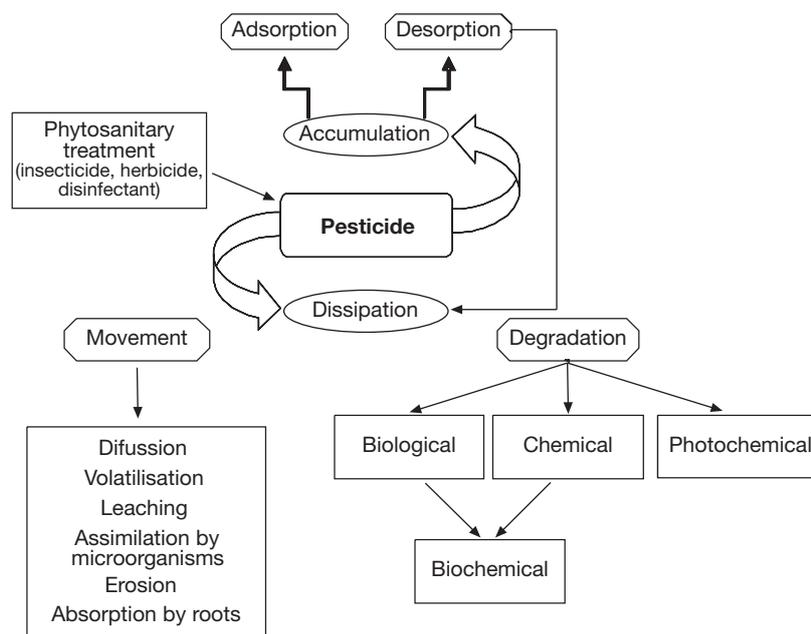


Figure 2. Schematic representation of pesticide dynamics in soil.

and Barba, 1996). From the physical-chemical data of adsorption, mobility and degradation obtained in the laboratory, it is possible to predict with a high degree of reliability the behaviour of pesticide in the soil.

Processes responsible for accumulation of pesticides in the soil: adsorption-desorption

The process of adsorption, which may be chemical in nature (as with electrostatic interactions) or purely physical (as with van der Waals forces), is a phenomenon whereby the molecules of a fluid come up against a solid surface and are retained on it at a given time, establishing a partition balance. This concept is applicable to the case of pesticides. In this case, adsorption is the result of the electrical attraction between charged particles, pesticide molecules (sorbate) and soil particles (adsorbent). Frequently, pesticide molecules that are positively charged are attracted and can bind to negatively charged particles of clay and organic matter. The extent of adsorption depends on the properties of soil and the compound, which include size, shape, configuration, molecular structure, chemical functions, solubility, polarity, polarizability and charge distribution of interacting species, and the acid-base nature of the pesticide molecule (Senesi, 1992; Pignatello and Xing, 1996). Soil pH, or the acid/base balance of the soil solution, affects the chemical's reactivity and certain soil func-

tions such as microbial metabolism. In the late 1960s, Weber *et al.* (1969) working with s-triazine herbicides provided compelling evidence to show that maximum adsorption of basic compounds occurs at pH values to their pK_a value. Acidic and anionic pesticides, such as phenoxyacetic acids (2,4-D and 2,4,5-T) and esters, asulam and dicamba, can interact with soil organic matter by H-bonding at pH values below their pK_a in non-ionised forms through their $-COOH$, $-COOR$ and identical groups (Senesi *et al.*, 1984).

Chemical reactions between unaltered pesticides or their metabolites often lead to the formation of strong bonds (chemisorption), resulting in an increase in the persistence of the residues in the soil, while causing it to lose its chemical identity (Dec and Bollag, 1997). From a toxicological point of view, binding of xenobiotics to humus lead to a decrease of material available to interact with biota, a reduction in the toxicity of the compound, and immobilising the pesticide, thereby reducing its leaching and transport properties. The nature of the binding forces involved and the types of mechanisms operating in the adsorption processes of pesticides onto the soil include ionic, hydrogen and covalent bonding, charge transfer or electron donor-acceptor mechanisms, van der Waals forces, ligand exchange, and hydrophobic bonding or partitioning (Gevao *et al.*, 2000b).

The relation between the concentrations of the compound in the solid and liquid phases is known as

the distribution coefficient and is directly proportional to the solubility of the pesticide in water and inversely proportional to the organic matter (OM) and clay content of the soil.

$$K_d = C_a/C_d$$

where K_d = coefficient of partition between soil and water (V/M); C_a = amount of pesticide adsorbed per unit of adsorbent mass (M/M); and C_d = concentration of pesticide dissolved (M/V).

Several methods have been proposed to measure the coefficient of distribution or partition (Karickhoff and Brown, 1978; Veith *et al.*, 1979). Karickhoff *et al.* (1979) demonstrated the existence of a lineal correlation between the coefficient of partition and the soil's organic carbon content:

$$K_{oc} = K_d / OC \cdot 100$$

where K_{oc} = soil organic partition coefficient; and OC the organic carbon content (%).

For polar molecules and soils with a low OM content and high clay content, Hermosín and Cornejo (1994) found a similar correlation:

$$K_{cc} = K_d / CC \cdot 100$$

where K_{cc} = clay content partition coefficient; and CC = clay content (%).

Both K_{oc} and K_{cc} are lineally correlated with the coefficient of partition between octanol and water (K_{ow}), which indicates the affinity degree of the pesticide for water (low value) or for soil (high value). Several studies have shown that the values of K_d are directly related with the concentration of pesticide in soil (O'Connor and Connolly, 1980; Voice *et al.*, 1983; Gschwend and Wu, 1985).

If the adsorption process is very intense, the molecule will not be bioavailable and its biological activity will decrease as a consequence. Furthermore, it will not be biodegradable and its persistence in the soil will increase; finally its mobility will diminish to a great extent as will its ability to contaminate ground waters. But if the soil conditions vary (moisture content, temperature, etc.), the compound may be desorbed and pass to the soil solution again, with attendant biocide risks. Hence, the difference between chemical and agronomic persistence.

One of the most widely used experimental techniques for evaluating the interaction of pesticides in soil, especially with the colloidal fractions, is to determine its adsorption isotherm, by which it is meant the relation

between the concentration of the compound adsorbed (C_a) and the concentration in equilibrium (C_e) at a constant temperature (Konda *et al.*, 2002). Giles *et al.* (1960) classified four different isotherms according to their geometric shape: L (normal or Langmuir), S (cooperative adsorption), C (constant distribution), and H (high density).

Several models have been developed to concrete the adsorption isotherms. The most used are those described by Freundlich (1909) and Langmuir (1918):

$$\text{Freundlich's model: } \ln C_a = \ln K + n \ln C_e$$

where K and n are constants related with the capacity and intensity of the process.

$$\text{Langmuir's model: } C_e/C_a = C_e/C_m + 1/C_m K$$

where C_m is the quantity adsorbed and K a constant related with the adsorption energy.

It must be borne in mind that since the soil is a complex system, many laboratory experiments are carried out in clays, oxides and/or organic matter, and the results are then extrapolated to the soil.

In the same way as adsorption, desorption can also be valued by means of isotherms obtained from the concentration that remains adsorbed by the soil in successive desorptions compared with the pesticide concentration in the equilibrium solution; once again, the models described by Freundlich (1909) and Langmuir (1918), among others, can be used. If the processes of adsorption and desorption do not occur to a similar extent, hysteresis is said to exist and this phenomenon can be evaluated by the difference between the quantities adsorbed and desorbed. The coefficients of hysteresis (%H) can be calculated in different ways, one being the way proposed by Hermosín *et al.* (1991):

$$\%H = (K_{des} - K_{ads}) / K_{des} \cdot 100$$

where K_{des} and K_{ads} are the adsorption and desorption coefficients obtained after fitting the adsorption isotherms to Freundlich's model.

Processes responsible for movement of pesticides in the soil

Pesticide transfer refers to the movement of pesticides from their site of application. Five processes than can move pesticides are diffusion, volatilization, leaching, erosion and run-off, assimilation by microorganisms, and absorption by plants.

— Diffusion

By this process a pesticide is transferred through the soil from one zone where it is more concentrated to another where it is less so, following Fick's law, according to which the net number of particle that cross a given area per unit of time is proportional and has the opposite sign from the concentration gradient. This phenomenon can be verified in the gaseous and liquid phases, or in the air of the intersolid phase. The coefficient of diffusion, solubility and steam pressure of the pesticide and, especially, the temperature, moisture and porosity of the soil and the degree of adsorption of the compound are the principal factors that influence this process.

— Volatilization

Volatilization is defined as the process by which a compound evaporates to the atmosphere from another environmental compartment. The volatilization of pesticides from the soil and their subsequent dispersion in the atmosphere is a common occurrence. Once volatilized, a pesticide can move in air currents away from the treated surface, a phenomenon known as vapour drift. Vapour drift differs from dust or spray drift in that it occurs after the pesticide is completely deposited onto treated surfaces. Volatilization is perhaps the most important route by which pesticides dissipate. The ecological and economic importance of this process is reflected by the amount of research carried out into the topic in recent years (Gan *et al.*, 1998; Majewski, 1999; Schroll *et al.*, 1999; Neumans *et al.*, 2000; Voutsas *et al.*, 2005). The results show that the potential volatility of a pesticide is closely related with its vapour pressure, the pressure exerted by the vapour of a compound on its own solid or liquid surface at equilibrium, although it also depends on soil temperature, colloidal composition, porosity, structure, water content and pH, and on the nature and concentration of the pesticide in the soil, together with its degree of adsorption. High temperatures favour the process, the only exception being when the soil dries quickly. The water content of the soil is also important: pesticides vaporize more quickly in moist than in dry soils. It should be noted that pesticides showing physical (weak) adsorption volatilise much more readily than those showing strong (chemical) adsorption since they are easily substituted by water molecules.

Volatilization from water, that is, partition of a substance between aqueous solution and the atmosphere, is subject to Henry's Law. This law states that, at equilibrium, the concentration of a chemical in the vapour state bears a constant relation to the concentration in aqueous solution. As regards this process, pesticides can be classified into two groups, according to their Henry's constant (K_H , the tendency of a material to volatilise from aqueous solution to air; sometimes measures, more usually calculated, as the ratio of vapour pressure—in pascals— x molecular weight/solubility in mg L^{-1}): those with K_H values of $> 10^{-5}$, which disappear rapidly from the soil, and those with K_H values of $< 10^{-5}$, which accumulate in the soil surface since the layer of stationary air acts as a barrier.

— Leaching

Much attention has been given to the use of pesticides in the field and the risk of pollution of ground and surface water (Spliid *et al.*, 2006). Pesticides that readily leach beyond the root zone of the soil are suspected to have the greatest potential to pollute ground water. Pesticides are frequently leached through the soil by the effect of rain or irrigation water but, for this to happen, the product must be sufficiently soluble in water. The pesticide may be displaced in solution or suspended in the water, or simply be emulsified. The process can be quantified to a certain extent in the laboratory by means of experiments using soil columns to which the pesticide being studied is applied or by thin layer chromatography, depending on the nature of the product used and, particularly, on the colloidal composition of the soil and its potential to act as adsorbent. Thus, Oliva *et al.* (2000) showed the differing behaviour of the herbicides propyzamide and benfluralin when they are applied to the soil in identical conditions. The breakdown curves obtained indicated the much greater mobility for propyzamide, which is directly related with the water solubility of both compounds (15 mg L^{-1} and 0.1 mg L^{-1} for propyzamide and benfluralin, respectively). Other experimental results have shown that in the case of some pesticides, such as simazine, the addition of organic amendment to a soil reduces leaching considerably since the adsorption of the herbicide is increased (Cox *et al.*, 1998). Several models simulating the vertical one-dimensional movement of pesticides, through the soil profile have been recently used in the European Union (Vancloster *et al.*, 2000). The relative mobility (leaching distance)

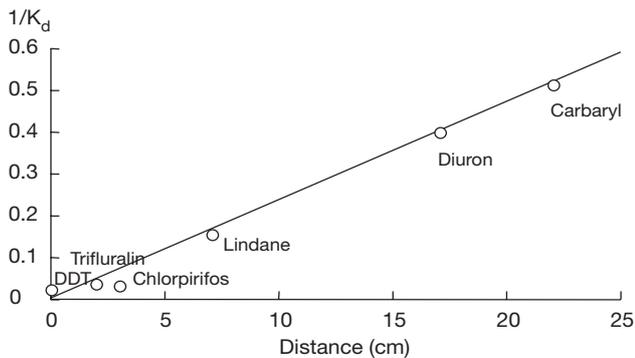


Figure 3. Relation between leaching distance of several pesticides and their coefficient of distribution (K_d) in the soil (adapted from McCall *et al.*, 1981).

is inversely proportional to the coefficient of distribution (K_d) in the soil. Therefore hydrophobic products, such as DDT, remain on the soil surface longer, while other, more water-soluble products, such as carbaryl or diuron, are more liable to leach (see Fig. 3).

— Erosion and run-off

Erosion includes two processes which limit each other: the destruction of soil aggregates and the displacement of the resulting fractions, which are exposed to transport by water, wind or living things (Giráldez, 1998). Pesticides deposited in a soil remain closely bound to it, whether it be by adsorption or through simple mixing. The soil, therefore, acts as conveyor of the pesticide when its particles are moved from one place to another through the effects of wind or run-off, leading in certain cases to the contamination of surface waters (rivers, seas, lakes). A variety of factors intervene in this process, among the most important being the soil slope, the formulation of the pesticide and the time since its application, the soil's structural stability and the type of plant cover, rainfall intensity, and the physico-chemical characteristics of the molecule in question and its degree of adsorption. In general, pesticide losses in run-off are most likely to occur when a heavy rainfall or excessive irrigation takes place shortly after a pesticide is applied to the soil surface.

— Assimilation by microorganisms in the soil

Agricultural soils contain many organisms which, as their life cycle develops, degrade or absorb certain

pesticides, so that they may well contain higher pesticide concentrations than the environment. Absorption of pesticides by target and nontarget organisms is quite variable and is influenced by species characteristics, environmental conditions, and by the chemical and physical properties of both the pesticide and the soil. Some authors (Gevao *et al.*, 2000a) have demonstrated that the bound residue formation is retarded in soils containing earthworms for some pesticide such as isoproturon, dicamba and atrazine. To determine the probability of a pesticide being absorbed and distributed by a given organism, it is useful to know its coefficient of partition between octanol and water (K_{ow}), by which is understood the ratio existing in the balance between the molar concentrations of the substance dissolved in a two-phase system (octanol and water), this value being constant for each pesticide at a given temperature. It is usually expressed as a decimal logarithm ($\log K_{ow}$). A high coefficient indicates that the product will probably accumulate in living organisms, influencing the nature of the bond with the biological receptors. A low value, on the other hand, diminishes the possibility of bioaccumulation (Voice *et al.*, 1983; Gschwend and Wu, 1985).

— Absorption by plants

Several studies have shown how crops grown in areas previously treated with pesticides may absorb some compounds from the soil in concentrations that depend on a series of factors, including crop type, the physico-chemical properties of the compound used, climate, soil type and degree of contamination. Once absorbed, pesticides can be stored inside or broken down in other products with more or less toxicity than the parent compound. Also to be borne in mind are the effects that pesticide absorption by plants might have on the chemical composition and yield of the same. For example, the application of aldicarb to the soil to combat insects and nematodes, significantly increases leaf concentration of soluble sugars at the same time as it decreases the protein content and nitrate reductase activity in the same organs (Balayannis, 1983).

When pesticide-treated plants are removed from an area, any pesticide residues they contain are removed with them. The ultimate fate of those residues is a function of how the plant is handled. For instance, food processing removes or degrades much of the remaining pesticide residues. On the other hand, composting of

the plant materials provide an excellent environment for pesticide degradation.

Processes responsible for disappearance of pesticides from the soil

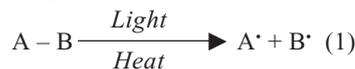
Together with movement, degradation is the other process responsible for the disappearance of pesticides in soil. Three processes merit special attention in this respect: photodecomposition or photochemical degradation, chemical degradation and biological degradation (biodegradation). Photochemical transformations occur commonly in the soil and they may totally destroy or appreciably modify a number of different types of pesticides. Nonenzymatic, nonphotochemical reactions are also prominent in soil, and they may bring about significant changes. However, such processes rarely convert pesticides to inorganic compounds in soils, and many of these reactions only bring about a slight modification of the molecule so that the metabolites are frequently similar in structure, and often in toxicity to their parent precursors. On the other hand, biological transformations, which involve enzyme as catalysts, frequently bring about extensive modification in the structure and toxicological properties of pesticides. In the case of organic compounds, biodegradation frequently, although not necessarily, leads to the conversion of much of the C, N, P, S, and other elements to inorganic compounds, process known as mineralization (Alexander, 1994).

— Photochemical degradation

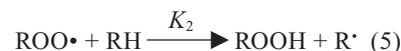
It is known that most pesticides show UV-Vis absorption bands at relatively short UV wavelengths. Since sunlight reaching the earth's surface (mainly UV-A, with varying amounts of UV-B) contains a very small amount of short wave-length UV radiation, the direct photodegradation of pesticides by sunlight is expected to be, in general, of only limited importance. The process begins when the pesticide molecule receives energy (Table 1); this excites the molecules in such a way that they either break up or form less stable bonds. Photolysis can be direct, when the pesticide receives UV light within the spectrum of sunlight (< 300 nm), or indirect, when the energy is absorbed by other compounds which subsequently transmit it to the pesticide molecule or give rise to different reactive species. This has led to

Table 1. Scheme for stages of photochemical degradation

Initiation



Propagation



Termination



many studies into the different mechanisms by which pesticides can be photo-degraded both in soil and water (Zeep and Cline, 1977; Dureja and Chattopadhyay, 1995; Romero *et al.*, 1995; Cheng and Hwang, 1996; Pirisi *et al.*, 1996; Conceição *et al.*, 2000; Konstantinou *et al.*, 2001; Frank *et al.*, 2002; Graebing *et al.*, 2003). Both direct and indirect process could be occurring depending on the depth. Herber and Miller (1990) concluded that the vertical depth of direct photolysis on the soil surface will be restricted to a region of approximately 0.2-0.3 mm while mean indirect photolysis has been reported to be greater than 0.7 mm for outdoor experiments. The principal factors in the process are the presence of photochemical catalysts, the intensity and length of exposure to radiation, soil pH and aeration, chemical structure and physical state of the pesticide and degree of colloid adsorption. According to Konstantinou *et al.* (2001), the humic acids are capable of acting as sensitizers for the production of reactive intermediates such as singlet oxygen (1O_2), hydroxyl radicals ($\cdot OH$), hydrogen peroxide (H_2O_2), and peroxy radicals ($ROO \cdot$). Also, metal oxides presented in the soil, such as ZnO, Fe_2O_3 and MnO_2 absorb radiation in the sunlight wavelength range and could accelerate degradation by reaction of ($\cdot OH$) and ($\cdot O_2$) through the well-known mechanism of semiconductor photochemistry. A detailed and exhaustive review about the photoreactivity of pesticides under both solar and ultraviolet irradiation can be seen in the article by Burrows *et al.* (2002).

— Biochemical degradation

At the outset we should differentiate between chemical and biological degradation, although in many cases both processes are closely linked and it is difficult to distinguish between them. To do so, it is necessary to eliminate the microorganisms in the soil by suitable radiation or sterilisation techniques, which also implies altering other catalytic systems that strongly influence degradation. Both processes therefore are usually treated together as biochemical degradation.

The transformations that pesticides may undergo in the soil are many and varied, and depend not only on the characteristics of the pesticide but on the colloidal composition, texture and moisture content of the soil, the number of microorganisms present, etc.

Many of the reactions that pesticides undergo in soil and water are largely catalysed by microorganisms, including bacteria and fungi, which are capable of degrading them, giving rise to a great variety of metabolic products. Thus, some microorganisms are capable of using certain pesticides as their only source of carbon and nitrogen, for example *Pseudomonas* (with 2,4-D and paraquat), *Nocardia* (with dalapon and propanyl) or *Aspergillus* (with trifluralin and picloram) (Higgins and Burns, 1975). Also the increase in microbial activity with atrazine pollution was noticeable after lengthy incubation (Moreno *et al.*, 2007). In some cases, the photochemical pre-treatment integrated with microbial degradation lead to the complete degradation and detoxication of some pesticides as occurs with atrazine (Chan *et al.*, 2004).

According to Alexander (1994), several conditions must be satisfied for biodegradation to take place in the soil. These include the following: 1) the organism must be present in the soil containing the pesticide, 2) an organism must have the necessary enzymes to bring about the biodegradation, 3) the pesticide must be accessible to the organism having the requisite enzymes, 4) if the initial enzyme bringing about degradation is extracellular, the bonds acted upon by that enzyme must be exposed for the catalyst to function, 5) should the enzymes catalyzing the initial degradation be intracellular, that molecule must penetrate the surface of the cell to the internal sites where the enzyme acts, and 6) because the population or biomass of bacteria or fungi acting on many synthetic compounds is initially small, conditions in the soil must be conducive to allow proliferation of the potentially active microorganisms.

The most important role of microorganisms in the transformation of pesticides is their ability to bring about *detoxication* (sometimes designated detoxification). Detoxications result in inactivation, with the toxicologically active ingredient being converted to an inactive product, because toxicological activity is associated with many chemical entities, substituents, and modes of action, detoxications similarly include a large array of different types of reactions (Table 2).

On the contrary, one of the more surprising, and possibly the most undesirable, aspects of microbial transformations in the soil is the formation of toxicants. Some pesticides that are themselves innocuous can be converted to products that may be harmful to humans,

Table 2. Most common biochemical transformations in water-soil ecosystems

Oxidation	$\text{RCH}_3 \rightarrow \text{RCH}_2\text{OH}$
Oxidative dealquilation	$\text{ROCH}_3 \rightarrow \text{ROH} + \text{HCHO}$
Decarboxylation	$\text{RCOOH} \rightarrow \text{R-H} + \text{CO}_2$
Aromatic hydroxylation	$\text{Ar} \rightarrow \text{ArOH}$
Ring rupture	$\text{Ar(OH)}_2 \rightarrow \text{CHOCHCHCOHCOOH}$
β -oxidation	$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} \rightarrow \text{CH}_3\text{COOH} + \text{CH}_3\text{COOH}$
Epoxidation	$\text{RC} = \text{CR} \rightarrow \begin{array}{c} \text{RC-CR} \\ \diagdown \quad \diagup \\ \text{O} \end{array}$
Oxidation of compounds with S	$\text{R}_2\text{S} \rightarrow \text{R}_2\text{SO}$
Oxidation of amino acids	$\text{RNH}_2 \rightarrow \text{RNO}_2$
Hydrolytic dehalogenation	$\text{RCHClCH}_3 \rightarrow \text{RCHOHCH}_3 + \text{Cl}^-$
Reductive dehalogenation	$\text{RCCl}_2\text{R} \rightarrow \text{RCHClR} + \text{Cl}^-$
Dehydrohalogenation	$\text{RCH}_2\text{CHClCH}_3 \rightarrow \text{RHC} = \text{CHCH}_3$
Nitroreduction	$\text{RNO}_2 \rightarrow \text{RNH}_2$

animals, plants, and microorganisms. The process of forming toxic compounds from innocuous precursors is known as *activation*. The conversion may represent a single reaction or a sequence in a cometabolic process. Alternatively, the harmful metabolite may be an intermediate in mineralization, yet it may persist long enough to create a pollution problem. The consequences of activation include the biosynthesis of carcinogens, mutagens, teratogens, neurotoxins, phytotoxins, and insecticidal and fungicidal agents (Alexander, 1994). Many different mechanisms are associated with activation such as nitrosamine formation, dehalogenation, epoxidation, conversion of phosphorothionate to phosphate, oxidation of thioethers, hydrolysis of esters and others.

— Kinetics of pesticide degradation

Knowledge of the kinetics of biochemical degradation is essential to the evaluation of the persistence of pesticides and to assess exposure of humans, animals and plants. Given the array of chemicals, the complexity of some environments, and a variety of microorganisms that may bring about biodegradation, it is unlikely that a single model or equation would be useful for the description of rates of the pesticides losses in the soil. Research on kinetics has focused on two topics. The first is assessing factors that affect the amounts of pesticides transformed per unit time as influenced by temperature, pH, moisture of the soil, and other C sources on the rates of losses. The second topic is determining the shapes of the curves that depict the transformation and evaluating which of the patterns of decomposition best fit the metabolism of given compounds in a microbial culture, in laboratory microcosms, and even in the field (Alexander, 1994).

Although many factors as above mentioned influence the disappearance of pesticides from soil, most of the models proposed consider the pesticide concentration as the only dependent variable (Timme and Frehse, 1980; Timme *et al.*, 1986). For this reason, when representing the evolution of residues *vs* time elapsed since application of the phytosanitary treatment an exponential type graph is obtained (Fig. 4), according to the following equation:

$$R_t = R_0 e^{(-Kt)}$$

where R_t is the residue at time t ; R_0 is the residue at time zero; K , the rate constant for chemical disappearance and t , the time elapsed since application.

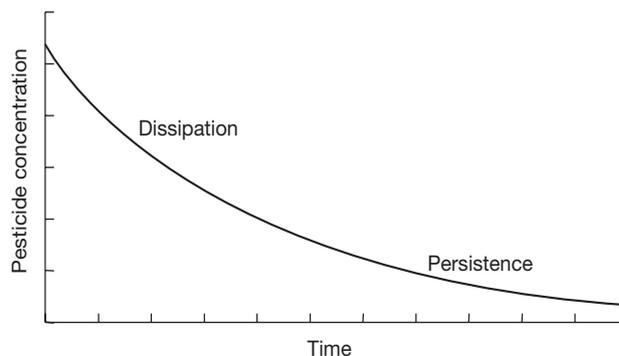


Figure 4. Typical pesticide dissipation curve.

First-order degradation is to be expected when the microorganisms are not in abundance in the soil, possibly because nutrient limitation. A common way of presenting first-order kinetics is to plot the logarithm of the pesticide concentration as a function of time; if the reaction is first order, a straight line is obtained according to the following expression:

$$\ln R_t = \ln R_0 - Kt$$

Once the constant K has been calculated, the half life time can be calculated using the following expression:

$$t_{1/2} = \ln 2/K$$

With this expression the persistence in the soil of the different pesticides can be compared.

Bound residues: concept and environmental significance

The number of metabolites or residual products that appear with photochemical and biochemical degradations is very high because of the large number of pesticides with different characteristics. These new structures can be incorporated by polymerisation in the humic substances of the soil, giving rise to others of great stability (Fig. 5).

The terms *free* and *bound* residues were coined to indicate that the former can be readily extracted from soil without altering their chemical structures, whereas the latter are resistant to such extraction (Gevao *et al.*, 2000b). However, the distinction between these two fractions is not always clear, because while they are in the soil, even the extractable residues are not entirely free from any form of binding because they may be

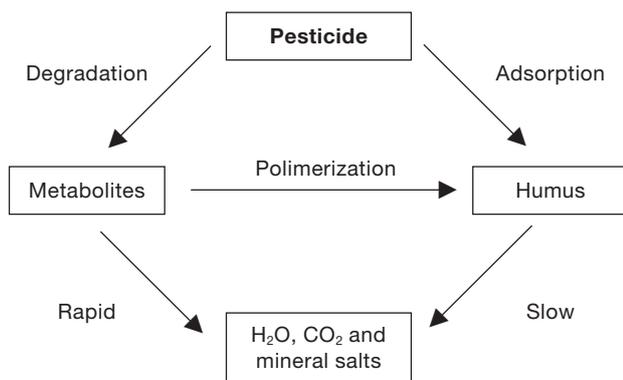


Figure 5. Schematic representation of pesticide degradation in soil.

sorbed to the soil solid phases and, therefore, show reduced bioavailability and degradation.

According to Roberts (1984), bound residues are «chemical species originating from pesticides, used according to good agricultural practice, that are unextracted by methods which do not significantly change the chemical nature of these residues». Twelve years later, according to IUPAC, a modification to the existing definition of bound residues was proposed by Fuhr *et al.* (1998): compounds in soils, plants or animals which persist in the matrix in the form of the parent substance or its metabolite(s) after extraction.

Depending on the nature of binding, immobilised pesticides may be released back to the soil solution or mineralized as a result of changing environmental conditions in the soil (Khan, 1982). The environmental significance of a bound residue depends not on its non-extractability under laboratory conditions, but on its bioavailability (Calderbank, 1989). According to Khan (1982), the bioavailable bound residue is the fraction of a pesticide in soils which can be taken up by plants and/or soil-inhabiting animals, while the non-available fraction cannot.

Several agricultural and environmental factors are capable of influencing the fate and binding of pesticides in soil. Among them we can mention the following: 1) *pesticide concentration*; persistence of pesticides in soils has been found to increase with increasing of concentration, whereas mineralization, metabolization and bound residues decrease at higher concentrations (Racke and Lichtenstein, 1987; Gan *et al.*, 1995), 2) *repeat applications*; some studies reported an increase in the formation of bound residues with repeated pesticide treatments (Khan and Hamilton, 1980; Zhang *et al.*, 1984), 3) *ageing*, referred as the increase contact time

between a chemical and soil, leading to the formation of a larger proportion of pesticides retained permanently in soil and therefore, tend to lose their biological activity and become even more resistant to degradation and extraction (Gevao *et al.*, 2000b; Reid *et al.*, 2000), 4) *addition of soil amendments*; soil amendments with organic materials have been reported to alter the fate and kinetics of chemicals added to soils (Morillo *et al.*, 2002; Navarro *et al.*, 2003), and 5) *mode of application to soil*; the amount of bound residues formed in soils has been found to vary with the methods used for pesticide application, with a higher proportion of bound residues formed if pesticides are uniformly applied into the soil as opposed to surface applications because uniform treatment reduce pesticide losses by volatilisation and runoff.

The process of bound residue formation of pesticides and other xenobiotics is highly complex and requires further research to establish their mechanisms and subsequent environmental and toxicological fate (Craven, 2000; Northcott and Jones, 2000). The ability of the soil to retain these compounds is due to adsorption phenomena and chemical reactions occurring on the active surfaces on mineral particles and humus.

There is concern at the moment about whether the formation of bound residues is an environmental solution or a problem (Barraclough *et al.*, 2005). In general, the formation of bound residues is considered an effective method for soil decontamination since the complex structures formed inactivate the original compound. Many years ago, as early as 1957, it was reported that ageing of pesticides in soils results in the loss of toxicity (Edwards *et al.*, 1957). More recent studies have verified that toxic chemicals residing in soil become less toxic with time (Hatzinger and Alexander, 1995; White *et al.*, 1997). The available data indicate that the microbial release of bound pesticide residues occurs extremely slowly. The relevance of the release is whether released residues are of toxicological or ecological significance. It is thought that the activity of microorganisms is the primary factor responsible for the release of bound residues. Other factors implicated are changes in agricultural practices and the introduction of certain chemicals that may change the biochemistry of soil (Gevao *et al.*, 2000b). When pesticide residues are released they can be mineralised, re-incorporated into humus and released into soil solution to their uptake by plants, soil biotic community or leached into ground water. It can be suggested

that effects on biota can only be noticeable when concentrations of bound residues are sufficiently high (Scheunert *et al.*, 1995).

Clean-up of pesticide contaminated soils

Several strategies are followed for remediation of soils contaminated by pesticides where feasible, pesticide-polluted soils are spread on agricultural land at labelled rates (Paulson, 1998). Alternatively, the soil may be excavated and shipped to a certified landfill or incinerated. The cost of these methods is often prohibitive and may pose many environmental concerns. Therefore, alternative low-cost and easy methods are needed to accelerate the degradation and natural attenuation of pesticides from multiple chemical classes. Among them, *bioremediation*, *use of zerovalent iron* and/or *soil biosolarization* have been proposed in the last years as alternative for the reduction or elimination of pesticide residues in soils.

Bioremediation as strategy to soil detoxication

Citizens around the world recognize the urgent necessity to do something to restore the environment to a safe and healthy state, due to the diversity of anthropogenic and naturally hazardous chemicals release, purposely or accidentally, to soils. Bioremediation is a relatively cleanup approach gaining favour in the last two decades. Bioremediation is a general concept that includes all those processes and actions that take place in order to biotransform an environment, altered by contaminants, to its original status. According to Bollag and Bollag (1995), bioremediation is the use of microorganisms or plants to detoxify an environment, mostly by transforming or degrading xenobiotics. Four basic techniques may be used: i) stimulation of the activity of the indigenous microorganisms by the addition of nutrients, regulation of redox conditions, optimizing pH conditions, etc., ii) inoculation of the sites with microorganisms of specific biotransforming abilities, iii) application of immobilized enzymes, and iv) use of plants (phytoremediation) to remove, contain, or transform pollutants. The utility of bioremediation in the degradation of pollutants in the environment has

been successfully demonstrated for several xenobiotics, including pesticides (Singh *et al.*, 2006). In the specific methods used for biorremediating contaminated soil and water, landfarming, composting, intrinsic bioremediation and slurry bioreactor are included (Thassitou and Arvanitoyannis, 2001).

From an engineering perspective, *landfarming* is a managed treatment and ultimate disposal process that involves the controlled application of a waste to a soil or soil-vegetation system (Loehr *et al.*, 1985). The biodegradation conditions by the natural indigenous microbial populations of soils are optimized by dilution of contaminated soil with clean soil, tilling of the soil to reduce initial toxicity, as well by controlling physical parameters, such as aeration, pH, soil moisture content, and temperature.

Composting is a biological aerobic decomposition of organic materials in which conditions are strictly controlled in order to help thermophilic microorganisms to transform organic materials into stable, soil-like product. A composting-like process occurs in the environment when materials are decomposed by microorganisms present in the soil although the decomposition rates are slow. In order to achieve maximum efficiency, some conditions such as oxygen concentration, pH, moisture content, C/N ratio and particle size need to be optimized (Miller, 1993).

One of the most important treatments of bioremediation is *in-situ* treatment of soils. This is a natural process occurring ever since the first microbes and excess organic matter were both present in the soil (Litchfield, 1993). The decomposition of the contaminants is carried out by the indigenous microorganisms which grow on a determined polluted soil by using contaminating compounds as a source of energy being forced by the environmental conditions to adapt or die or having been genetically modified (Ellis and Gorder, 1997).

Finally, in slurry bioreactor treatment systems, the polluted soils are excavated and mixed with water to form slurry that is mechanically aerated in a reactor vessel. The slurry is agitated to promote breakdown of soil aggregates, enhanced desorption of pesticides, increased contact between the soil or wastes and microorganisms, and enhance oxygenation (Baker, 1994). Slurry bioreactors generally have a higher cost than the *in-situ* treatments because of the high degree of engineering involved although the biodegradation rates obtained are faster.

More details about principles, advantages, disadvantages, and applications of bioremediation methods can

be seen in the articles by Bollag and Bollag (1995) and Thassitou and Arvanitoyannis (2001).

Accelerated remediation with metals

Treatment with zerovalent iron (Fe^0) has been shown to promote reductive dechlorination of several pesticides (Eykholt and Davenport, 1998; Monson *et al.*, 1998; Comfort *et al.*, 2001; Dombek *et al.*, 2001; Shea *et al.*, 2004). The use of Fe^0 to treat pesticide-contaminated soils is based on the fact that many pesticides contain moieties that can be reduced when coupled to the oxidation of iron metal, with Fe^0 and Fe(II) serving as reductants playing pH a decisive role in the process. Some authors have shown that the combined use of Fe^0 and $\text{Al}_2(\text{SO}_4)_3$ and CH_3COOH enhanced degradation of several pesticides (Comfort *et al.*, 2001).

Soil biosolarization

Soil solarization is a disinfection method, first described by Katan *et al.* (1976), for controlling soilborne pathogens and weeds, mostly as a pre-planting soil treatment. This simple technique captures radiant energy from the sun, thereby causing physical, chemical, and biological changes in the soil (Katan and De Vay, 1991). Transparent polyethylene plastic placed on moist soil during the hot summer months increases soil temperatures to levels lethal to many soilborne plant pathogens, weed seeds, and seedlings, nematodes, and some soil residing mites. Soil solarization also improves plant nutrition and yield (Katan, 1981, 1998). Limited cloud covers in arid and semi-arid regions of the world result in shorter periods of solarization (4-6 weeks).

Plastic mulches have been used predominantly for management of soil moisture, temperature, nutrients, and weed control (Katan *et al.*, 1987). The use of this method on the persistence of pesticides has led to a variety of results. While ethiofencarb persisted longer in solarized soils, other as bromacil was not affected by this method but volatile herbicides EPTC and vernolate degraded rapidly (Yarden *et al.*, 1990). Also for quinalphos (organophosphorus insecticide) the rate of loss was higher in mulched soil (Gopal *et al.*, 2000).

On the other hand biofumigation refers to the use of plants containing biologically active compounds as

rotation crops or green manures to suppress soilborne pests and diseases in agricultural production systems. Some nematodes can be controlled successfully by soil solarization where solar radiation is sufficient. However, control of root-knot nematodes has proven difficult. Biofumigation has also been used for the control of soilborne diseases, but results also appear to be variable. For this, both are combined (biosolarization) for better results (Ploeg and Stapleton, 2001). The use of biosolarization enhanced dissipation of some pesticides as pirifenox (Flores *et al.*, 2006).

Conclusions

Soil contamination is the presence of man-made chemicals or other alteration to the natural soil environment. Human activity, especially during the twentieth century, has led to contamination of many sites with organic and inorganic compounds that pose a threat to human, animal, or plant health. Despite the wide ranging research carried out on this subject in recent years, we still only partially know how contaminants move through the atmosphere, soil and water, and how they are transformed during their transport.

Between 1,000 and 1,500 new chemical products are synthesised each year and it is estimated that approximately 60,000 are in daily use, much of them organic compounds (including pesticides). Research carried out in recent decades has greatly contributed to our knowledge of how these products behave in the environment. It is clear that their residual concentrations may well constitute in certain cases an important source of contamination in areas here they have been long used. From a knowledge of only four parameters (octanol/water partition coefficient, Henry's constant, dissociation constant and adsorption spectrum), it is possible to estimate and predict certain processes such as hydrolysis, photodegradation, volatilisation, adsorption and bio-concentration. However, much less has been learnt about one of the most important disappearance pathways, biotransformation.

The mobility of pesticides through air and/or water, their accumulation and/or transformation in the medium to which they are applied and, finally, their biomagnification, since they may be introduced into the food chain, increasing their concentration as they pass from one link in the chain to another, constitute a risk that must be compared with the possible benefits that they may provide.

Regarding to the formation of bound residue formation in soils, there are two viewpoints, one negative and other positive. The former is based in the fact that bound pesticide residues represent a hidden fraction of the parent compound or metabolites capable of subsequent release being able to cause ecological effects. The positive point of view is that the bound residues represent the most effective and safe method of decontamination of soils by rendering the molecule innocuous by slow degradation in the bound state.

At the present moment it is fundamental to apply strategies for remediation of soils contaminated by pesticides. Bioremediation, which involves the use of microbes to detoxify and degrade pollutants, has received increased attention in the last years as an effective biotechnological approach to clean up polluted environments. Other remediation techniques such as the treatment with metals or the use of biosolarization are also effective in some cases to remove pesticides from contaminated soils.

All the above clearly points to the need for pesticides to be used rationally by growers, organisations, distributors, etc., who must strictly observe the norms and recommendations governing their use. If this is done, application of these compounds do not necessarily will cause serious damage to the environment, as is borne out by the evidence from recent research.

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