

# The Fate of Herbicides in Soil

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## 1. Introduction

The agrochemical spreading is a common and essential agricultural practice to obtain high quality, large harvests.

Agrochemicals are classified according to the target organisms designed to be controlled (insects, weeds, fungi). Of all the target organisms, weeds cause by far the greatest economic loss due to their interference in crop production. It is not surprising therefore, that herbicides are the most common class of agrochemicals in the world (48% of the total expenditure) and in Europe (43%) outstripping fungicides (35%) and insecticides (14%). Europe, Asia, and the United States are the largest consumers of agrochemicals; in Europe, France has the biggest agricultural areas, and is the highest-ranking country for pesticide consumption followed by Germany and Italy (see <http://www.croplife.org/> and <http://www.ecpa.be>).

Bad agricultural practice and accidental spreading of high doses of agrochemicals can determine toxic effects in humans and the environment; pesticides can accumulate in organisms and achieve critical concentrations for the human and ecosystem health.

Agrochemicals were used for the treatment of human diseases like malaria and typhus. However, high doses of some pesticides can be highly toxic to humans. Laboratory experiments have shown that the administration of high doses of pesticides to animals can cause cancer, mutagenesis, and even death; moreover, exposure to low doses can cause skin irritation and breathing problems. In the “infamous” case of DDT, for instance, which was introduced onto the market in 1940 for the malaria and typhus control, the central nervous system was attacked causing loss of memory, tremblings, and personality changes. Paraquat, a dipyridylic herbicide, is an extremely toxic systemic pesticide; it can enter in the body by inhalation, ingestion or direct contact. It is especially toxic to the lungs, but can cause gastrointestinal apparatus, kidney, liver, and heart disorders and the weakening of other organs with vital functions.

Plants that are sensitive to pesticide molecules may show signs of growth inhibition and loss in biomass even as far as necrosis, but may be able to develop resistance to certain pesticides (see <http://www.weedscience.org>; Yuan et al, 2007). Agrochemicals may also have a toxic effect on nontarget plants (Madhun & Freed, 1990) when transported away from the treated site (soluble herbicides or surface erosion).

Soil and aquatic ecosystems contain a multitude of microorganisms. After pesticide spreading, microbial activity may be reduced. However, in some situations an enhancement in microbial activity may occur (Lewis et al., 1978; Pozo et al., 1994).

The leaching of soluble and highly mobile molecules, wilful discharge in underground wells and accidental dumping in water bodies contribute to water contamination. Carabias Martinez et al. (2000) monitored the concentration of fifteen herbicides selected owing to their frequency of use, the amounts used, their toxicity and their persistence in river basins in the provinces of Zamora and Salamanca (Spain). After six months, the presence of six out of the fifteen herbicides monitored, was detected at levels ranging from the detection limit to 1.2  $\mu\text{g}/\text{L}$ . The presence of these herbicides was related to agricultural activities as well as the kind of crop and its treatment period.

The prediction of herbicide movement and fate in soils represents an important strategy in limiting their environmental impact (Figure 1). Physical, chemical, and biological processes regulate herbicide mobility and degradation in soil: rainfall and irrigation water can move herbicides along the soil profile; sites negatively charged of clay mineral surfaces and/or organic matter can adsorb herbicides in their cationic form at soil pH; microbial activity can promote herbicide transformation. Different transfer and degradation processes which control the movement and the fate of pesticides in the environment are reported in the Table 1. Except physical processes, other processes depend on soil characteristics.

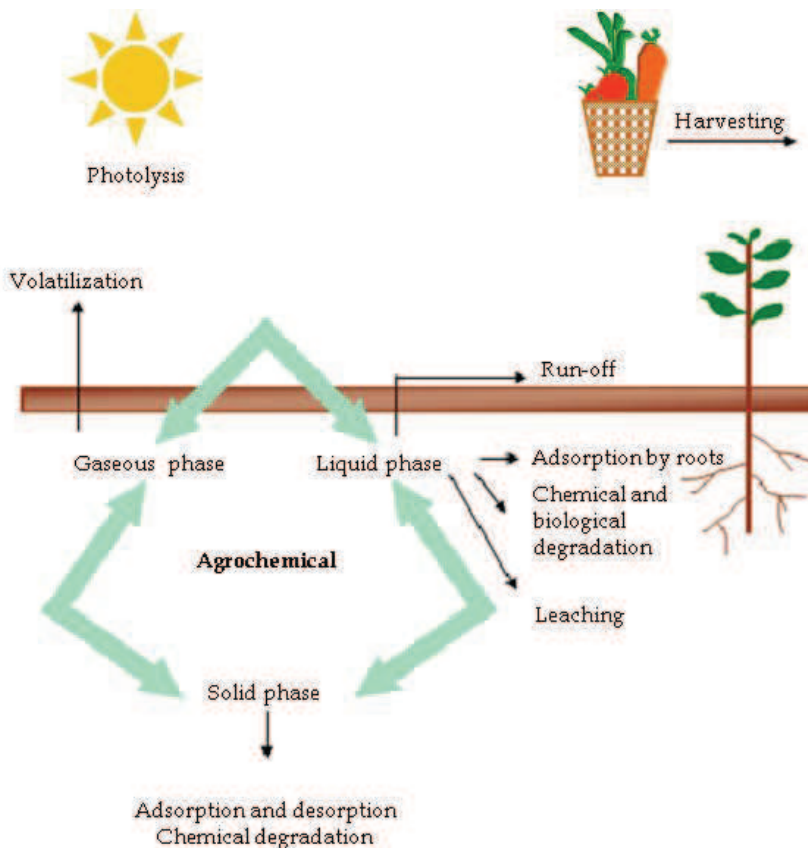


Fig. 1. The fate of agrochemicals in the environment.

Process	Consequence	Factors
<i>Movement (processes that relocate agrochemicals without changing their structure)</i>		
Physical drift	Movement due to wind action	Wind speed, drop sizes
Volatilization	Loss due to evaporation from soils, plants, and waters	Vapor pressure, wind speed, temperature
Adsorption	Removal due to interaction with soils, plants, and sediments	Clay content, organic matter, moisture
Absorption	Uptake by plant roots or animal ingestion	Cell membrane transport, contact time
Leaching	Horizontal and vertical movement downward through the soil	Water content, soil texture, clay and organic matter contents
Erosion	Wind and water action	Rainfall, wind speed, sizes of clay and organic matter
<i>Degradation (processes that modify the chemical structure)</i>		
Photochemical	Assorption of sunlight (i.e., ultraviolet radiation)	Chemical structure, intensity and duration of exposure
Microbial	Degradation by microorganisms	Environmental factors (pH, moisture, temperature) organic matter content
Chemical	Hydrolysis and redox reactions	pH modifications, same factors as microbial degradation
Metabolism	Adsorption by plants or animals	Adsorption capacity, metabolism, interactions with microorganisms

Table 1. Movement and degradation processes of agrochemicals in the environment (Pierzynski et al., 2000).

## 2. Chemico-physical parameters affecting the fate of herbicides in soil

The fate of herbicides such as that of any organic molecule released into the environment is determined by their chemico-physical characteristics.

*Solubility.* The solubility of an herbicide is important in predicting its behaviour in water and its mobility in soil. Agrochemical water solubility is a function of temperature, pH, and ionic strength and is affected by the presence of other organic substances such as the dissolved organic matter (DOM) (Pierzynsky et al., 2000). Two methods are frequently used to estimate organic molecule solubility based on i) chemical structure ( $K_{ps}$ ) and ii) the *n*-octanol/water partition coefficient ( $K_{OW}$ ). *n*-Octanol/water coefficients are determined by the following equation which highlights that there is an inverse relationship between solubility and  $K_{OW}$ :

$$K_{OW} = \frac{\text{concentration of organic chemical in octanol} \left( \frac{\text{mg}}{\text{L}} \right)}{\text{concentration of organic chemical in water} \left( \frac{\text{mg}}{\text{L}} \right)} \quad (1)$$

*Persistence.* The persistence of an herbicide is defined as the time in which the molecule remains in the soil and is usually expressed as half-life. Half-life ( $t_{1/2}$ ) refers to the time required to halve the organic molecule concentration compared with its initial level.

Half-life values are important in understanding the potential environmental impact of a chemical; in fact, a molecule which degrades quickly, has a low  $t_{1/2}$  value and thus the impact of this species on the environment is reduced if the degradation products are harmless. On the contrary, the environmental impact of species with a high  $t_{1/2}$  value can be substantial even if the molecule is only moderately toxic.

The prediction of herbicide half-life and thus, its persistence in the environment is an important parameter in agronomic practice because it supplies information on the residual activity of agrochemicals which could cause damages to the successive crops.

For a first order reaction, the half-life is determined by the following equation:

$$t_{1/2} = \frac{0.693}{k} \quad (2)$$

where  $k$  is the kinetic constant of the degradation reaction involving the agrochemical.

*Volatilization.* Volatilization of organic molecules is responsible for the transfer of molecules from aquatic and soil environments into the atmosphere. As with the solubility, it is important to know the contribution of agrochemical volatilization in predicting its residual amount and thus, its persistence in the environment.

The volatilization of herbicides from waters depends on the chemical and physical properties of the molecules in question (e.g., vapour pressure and solubility), their interaction with suspended materials and sediments, the physical properties of the water bodies (depth, turbulence, and velocity) and any water-atmosphere interface properties.

The solubility of a gas dissolved in an aqueous solution is well defined by the Henry constant, calculated using the homonymous equation:

$$K_H = \frac{P_{gas}}{C_{aq}} \quad (3)$$

where  $K_H$  is the Henry constant,  $P_{gas}$  is the gas partial pressure and  $C_{aq}$  is its concentration in the aqueous phase. For high  $K_H$  values, the molecule prefers to leave the liquid phase in order to pass into the atmosphere. This constant is useful to describe the agrochemical fugacity from a water body but also from soil solid components which are always surrounded by water in adsorbed form.

The rate of volatilization can be indicated as half-life, which is the time required to halve the organic molecule concentration in water compared with its initial value. The volatilization half-lives of different molecules are reported in the table 2.

Factors that influence the volatility of organic molecules from soils include the chemical and physiochemical properties of the pollutant (i.e., vapour pressure, solubility, the structure and nature of the functional groups, and adsorption-desorption characteristics),

concentration, soil properties (soil moisture content, porosity, density, and organic matter and clay contents) and environmental factors like temperature, humidity, and wind speed.

Volatilization	Agrochemical	$t_{1/2}$
<i>Low</i>	Dieldrin	327 d
	3-bromo-1-propanol	390 d
<i>Medium</i>	Phenantrene	31 h
	Pentachlorophenol	17 d
	DDT	45 h
	Aldrin	68 h
	Lindane	115 d
<i>High</i>	Benzene	2.7 h
	Toluene	2.9 h
	O-xylene	3.2 h
	Carbon tetrachloride	3.7 h

Table 2. Volatilization rates of some organic molecules (Pierzynsky et al., 2000).

*Photolysis.* Photochemical reactions involve sunlight radiation and play an important role in the degradation of molecules on soil surfaces and in aquatic environments. Photolysis in the soil is difficult to determine because of the heterogeneous nature of soils and low sunlight penetration. Nevertheless, it is an important herbicide degradation process in soil since it is always active.

In water as well as in soil, photolysis can occur either by direct or indirect processes. In direct photolysis, sunlight is absorbed directly by organic molecules which alter its chemical structure. The indirect process occurs in the presence of natural photosensitive species such as nitrates or humic acids which can absorb the light and subsequently transfer excitation energy to the organic molecule.

*Biodegradation.* Herbicide biodegradation is due to microorganism activity and is a function of those properties which influence microbial activity such as temperature and pH: a temperature or pH decrease slows down the biotic degradation rate since under such conditions microbial activity is reduced. This could explain the presence of certain molecules such as antibiotics, in the deeper layers of soils and waters (Gavalchin & Katz, 1994; Van Dijk & Keukens, 2000).

*Adsorption-desorption.* The ability of herbicides to adsorb on soils and sediments and their tendency to desorb are the most important factors affecting soil and water contamination. Adsorption depends on both molecule and soil chemico-physical properties. In soil, the surfaces responsible for adsorption are colloidal particles and among these, organic matter and clays. Organic matter, due to its chemical affinity with agrochemical molecules, has the greatest adsorption strength towards these species; high surface area and the interlayer charge of clays, such as expandable phyllosilicates, make these sorbents good for organic molecules.

Adsorption on clays or organic matter can occur with the following interactions: van der Waals forces, hydrogen bondings, dipole-dipole interactions, ionic exchange, covalent bondings, protonation, ligand exchange, cationic and H<sub>2</sub>O bridging, and/or hydrophobic interactions.

Cationic species adsorb on soil by electrostatic attraction while anionic molecules can adsorb on positively charged soil colloids, even if the adsorption of negative species is less strong than on the negatively charged clay surfaces. In acidic soils, herbicides which have amino groups can protonate to quaternary ammonium ions (-NH<sub>3</sub><sup>+</sup>) and form H-bonds with the oxygen atoms of the phyllosilicate surfaces or with nitrogen atoms of organic matter; molecules which have acidic functional groups remain in a neutral form (COOH).

Nonpolar molecules can interact with the hydrophobic moieties of soil organic matter: this hydrophobic bond is responsible for the strong adsorption of DDT and organochloride insecticides on soil organic matter.

The strength of adsorption affects molecule mobility along the soil profile and thus, its bioactivity, persistence, biodegradation, leaching, and the volatilization process. The adsorption of an agrochemical onto the soil components can be considered as the first step towards its chemical degradation.

Organic molecule adsorption modeling by soils is frequently done using adsorption isotherms.

Adsorption isotherms are built by measuring the residual concentrations of pollutant in aqueous solution at the equilibrium point, after the adsorption on soil of different initial concentrations. For each concentration point, the adsorbed molecule concentrations are determined by the difference between initial and equilibrium concentrations. Adsorption data are commonly fitted using two different models described by the Langmuir and Freundlich equations.

The Langmuir equation is:

$$\frac{x}{m} = \frac{K_1 b C}{1 + K_1 C} \quad (4)$$

where  $x/m$  is the mass of organic molecule adsorbed per unit of soil weight;  $C$  is the equilibrium concentration of the organic molecule;  $K_1$  is the Langmuir constant that is related to binding strength. The linear form of the Langmuir equation is:

$$\frac{C}{x/m} = \frac{1}{K_1 b} + \frac{C}{b} \quad (5)$$

If a plot of  $C/(x/m)$  vs  $C$  is a straight line, then the adsorption data satisfy the Langmuir equation, and  $b$  can be calculated from the slope and  $K_1$  from the intercept.

The Freundlich equation is:

$$\frac{x}{m} = K_f C^{1/n} \quad (6)$$

where  $x/m$  and  $C$  are the same as above;  $K_f$  and  $n$  are empirical constants.

The  $K_f$  value is a measure of the extent of adsorption whereas the  $1/n$  value indicates the affinity of organic molecule for the sorbent surface. If the  $1/n$  value is lower than 1, there is high affinity between the adsorbate and the adsorbent. If  $1/n$  is equal to 1, the solute is equally

distributed between the solution and adsorbent surface. If the  $1/n$  value is higher than 1, the adsorption is called “cooperative” because there is cooperation between the adsorbed molecules and the new molecules approaching the surface to promote the adsorption.

The linear form of the Freundlich equation is obtained by logarithmic transformation:

$$\log\left(\frac{x}{m}\right) = \log K_f + \frac{1}{n} \log C \quad (7)$$

A plot of  $\log(x/m)$  vs  $\log C$  should produce a straight line, with  $1/n$  being equal to the slope and  $K_f$  the intercept.

For many organic molecules, especially nonpolar species, adsorption can be constant, that is the adsorbed concentration is proportional to the equilibrium concentration. The Freundlich equation can be simplified:

$$K_d = \frac{x/m}{C} \quad (8)$$

where  $K_d$  is the distribution constant. The adsorption constant can be normalized to the organic carbon content of the soil ( $f_{OC} = OC\%/100$ ): the new constant is known as  $K_{OC}$  which is independent of soil type and specific to a given pollutant. The constant is calculated using the following equation:

$$K_{OC} = \frac{K_d}{f_{OC}} \quad (9)$$

*Adsorption isotherms.* Adsorption isotherms of organic molecules are divided into four classes, according to the nature of the initial curve portion (Giles et al., 1960). The four classes are known as H (high affinity), L (Langmuir type), C (constant partition), and S (sigmoidal or with an “s” form) isotherms (Figure 2). The L curves are the best known: the initial curvature shows that as more sites in the substrate are filled, it becomes increasingly difficult for solute to find an available vacant site. The H isotherm is a special case of L curve, where the solute has a high affinity for the surface especially at low concentrations. The C curves are characterized by the constant partition of solute between the liquid and solid phase; the constant partition is independent of concentration right up to the maximum possible adsorption, where an abrupt change in the slope to a horizontal plateau occurs. The initial part of the S curves describes contrary conditions in comparison with the other isotherms: the more solute has already been adsorbed, the easier it is for additional amounts to become fixed. This implies a side-by-side association between adsorbed molecules, helping to hold them to the surface. This has been called “cooperative adsorption”.

*Abiotic and biotic transformations.* Both abiotic and biotic reactions are responsible for the transformation of herbicides in soils and waters. One of the two processes may be dominant, but usually both of these participate simultaneously in molecule degradation. The principal abiotic reactions that occur in water are hydrolysis, oxidation-reduction, and photolysis; in sediments, hydrolysis and redox reactions may prevail. Redox reactions in aquatic environments can be mediated by direct or indirect photolysis or catalyzed by metal species. In soil, abiotic reactions occur in the liquid phase (i.e. soil solution) and at the solid-liquid interface. In soil solution, hydrolysis and redox reactions are the most common abiotic transformations; these reactions are catalyzed by clays, organic matter and metal oxides.

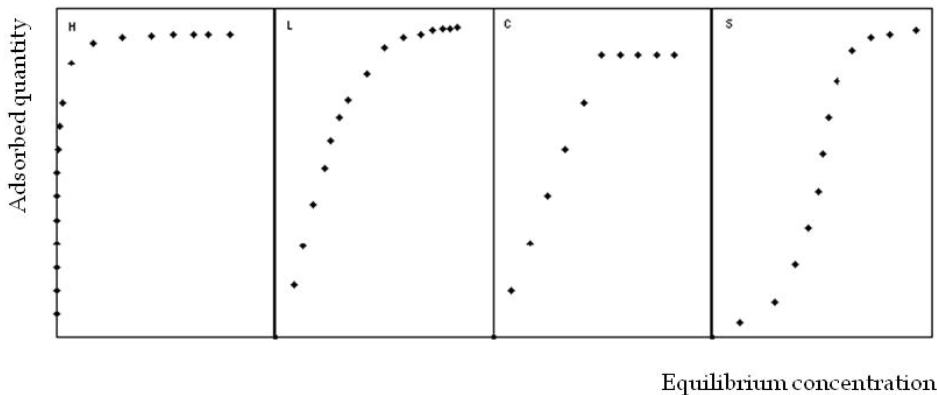


Fig. 2. The four main classes of isotherms. From left to right: high affinity (H), Langmuir (L), constant partition (C) and S curves.

Biotic reactions are classified as: i) biodegradation (contaminants are used as a substrate for microorganism growth); ii) cometabolism (contaminants are transformed by metabolic reactions without being used as an energy source); iii) accumulation (contaminants are accumulated in microorganisms); iv) polymerization or conjugation (contaminants are bonded to other organic molecules); v) secondary effects of microbial activity (contaminants are transformed by secondary microbial effects such as pH and redox changes) (Bollag & Liu, 1990).

Biodegradation is considered the principal mechanism for the conversion of organic molecules into  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and mineral salts.

Although these reactions are mediated by microorganisms, abiotic processes are also involved, especially in transformations related to categories iv) and v).

Braschi et al. (2000) have investigated the degradation of primisulfuron, a sulfonylurea herbicide, in microbial communities enriched with soils polluted by herbicide. The authors find that the degradation reaction of primisulfuron firstly occurs by means of hydrolysis and photolysis processes and that the role of microorganisms subsequently becomes important in the degradation of the herbicide metabolites.

### 3. Soil inorganic phase: clay minerals

Soil solid phases are almost totally characterized by inorganic components (fragments of rocks, primary and secondary minerals, amorphous materials); the organic component is only a small fraction.

Minerals are the most diffuse inorganic species in the lithosphere. From a chemical point of view, they are classified as: i) silicates formed by oxygen and silicon and ii) nonsilicates, such as oxides, carbonates, phosphates, sulphates.

Silicon tetrahedron is the building unit of silicates: different classes of silicates are obtained by the polymerization of building units.

Layered aluminosilicate minerals, known as clay minerals, have a profound influence on many soil chemical reactions because of their high active surface area. They have regular layers of tetrahedral and octahedral sheets: tetrahedral sheets are comprised of silicon and oxygen atoms with three out of every four oxygen atoms shared between adjacent



tetrahedra. There are two types of octahedral sheets: dioctahedral and trioctahedral. Dioctahedral sheets have two out of every three octahedral sites occupied, most often by the trivalent Al cation. Trioctahedral sheets have all octahedral sites occupied by divalent cations, which are commonly Mg ions. Clays have structures that are either 1:1, 2:1, or 2:1:1 layers of tetrahedral and octahedral sheets. 1:1 clay minerals have one tetrahedral and one octahedral sheet held together by sharing an apical tetrahedral oxygen. 2:1 clay minerals have an octahedral sheet posed between two tetrahedral sheets. 2:1:1 layered clays are similar to 2:1 clays with an additional dioctahedral or trioctahedral sheet between the 2:1 layers (Pierzynski et al., 2000).

The expansion property after water adsorption is typical to the 2:1 arrangement. In 1:1 clays, the oxygens of octahedral sheet bond with the oxygens of the tetrahedral sheet by means of H-bondings: this arrangement does not permit good expansion in water for this clay. In 2:1 clays, no hydrogen bonds are formed between the oxygens of tetrahedral and octahedral sheets; a weak repulsion develops and distributes over the surface, allowing the clay minerals to expand easily in water (Figure 3).

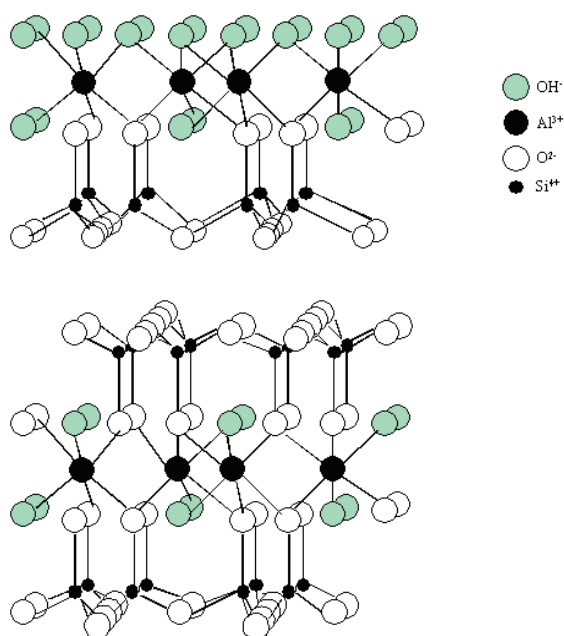


Fig. 3. Different arrangements of clay minerals: 1:1 on the top, 2:1 on the bottom.

Clay minerals contain active sites for adsorption which are localized in the tetrahedral sheet, and are formed by siloxanes (siloxane cavity). This cavity is bordered by six sets of lone-pair electrons (from the oxygen atoms) that give a nucleophilic character to the surface: polar or positively charged species can interact with this highly negative surface (Sposito, 1984). Water can occupy the siloxane cavity by pointing the hydroxylic group inside the cavity; the polarization induced by the surface, makes the water molecules strongly polarized and then reduces their mobility. The siloxane cavity extends along the whole tetrahedral sheet giving high adsorption properties to clays.

Clays can have a permanent negative charge which comes from *isomorphous substitutions* and a variable pH dependent charge. Isomorphous substitution occurs when an element substitutes for another in the mineral structure, such as  $\text{Al}^{3+}$  substituting  $\text{Si}^{4+}$ . If an element of a lower charge is substituted for an element of a higher charge, a permanent negative charge develops in the clay mineral: the net negative charge electrostatically attracts positive and polar species. The variable charge is due to the presence of surface hydroxylic groups that can lose or accept protons as a function of soil solution pH.

Cations in the soil solution are bonded to the surface of clay minerals by electrostatic interactions and can return in solution by the substitution of other cations or by dilution. The most representative exchange cations are  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Na}^+$ . Other cations, such as organic cations, are bonded onto clay minerals as a function of their affinity for the surface and their concentration in the soil solution.

Cations adsorbed onto clay surfaces are surrounded by hydration water. This water is more acidic than the water in the soil solution because cations attract the hydroxylic groups of water and move the water dissociation equilibrium towards higher values. This results in a decrease of 2-3 units of hydration sphere pH in comparison with the soil solution. The surface acidity effect is an important factor in the adsorption processes of herbicides which have nitrogen groups: in fact, the nitrogens contained in some agrochemical structures can be protonated by acidic surfaces and agrochemicals can be adsorbed by cationic exchange.

#### 4. Soil organic matter

The organic components of soils are characterized by:

- vegetable and animal residues which are partially degraded and *in transformation*;
- the biomass of living organisms;
- materials of the neogenesis.

Vegetable and animal residues are slowly decomposed by microbial attack on molecular and ionic compounds which can be transformed by polycondensation in macromolecules with complex and unknown chemical structures: these are known as humic substances.

Humic substances have colloidal dimensions, high specific areas and are able to adsorb molecules or ions. The dark colour of humic compounds promotes the sunlight radiation absorption and thus, the increase of soil temperature.

Organic matter plays an important role in the chemistry of soils: it covers the pores created by roots or pedofauna action by stabilizing the soil structure. Organic matter affects the water flow into the pores (capillary porosity): in fact, the coexistence of hydrophilic and hydrophobic properties in the same structure makes organic matter a material which is able to retain moisture or to repel the water by decreasing its flow along the pores. Moreover, organic matter forms macroscopic aggregates ("cements") with inorganic species (i.e. Fe and Al oxides and hydroxides) which stabilize the soil structure.

Finally, the organic matter can interact with agrochemicals by H-bondings, van der Waals forces,  $\text{H}_2\text{O}$  bridgings, and hydrophobic bondings.

#### 5. Dissolved organic matter, DOM

Dissolved organic matter (DOM) is defined as "the amount of organic matter that is able to dissolve in the field conditions". DOM plays an important role in the biogeochemistry of

carbon, nitrogen, and phosphorous, in pedogenesis and in the transport of pollutants in soils (Kalbitz et al., 2000).

The source of virtually all DOM in soils is photosynthesis; this includes both recent photosynthate (throughfall, leaf litter, root exudates, decaying fine roots) as well as the leaching and decomposition of older, microbially processed soil organic matter (McDowell, 2003). DOM ranges in age from hours to days, to decades and even up to thousands of years.

Sinks of DOM include microbial transformation and immobilization, mineralization (to CO<sub>2</sub>, inorganic N, etc.), precipitation, and adsorption on mineral surfaces.

Microbial soil communities are the most important agents in DOM formation. Guggenberger et al. (1994) studied DOM fractionation and structure and demonstrated that microbial metabolites constitute a significant portion of DOM. According to these studies, the carbohydrate fraction of DOM is chemically different from that in plant residues or bulk humus, in that DOM carbohydrates have a higher proportion of hexose- and deoxysugars than pentose sugars. Since pentose sugars are rarely found in microbial cells, DOM may be predominantly of microbial origin.

Zsolnay (1996) and Tipping (1998) have supposed that the DOM can be partitioned into mobile and an immobile fractions according to the pore sizes of the soil matrix. Only the mobile DOM fraction in macro- and mesopores is subjected to convective transport by seepage. DOM in micropores is immobile and interacts with the mobile fraction by diffusion.

Several field studies (Jardine et al., 1989; Michalzik et al., 2000) have shown that the DOM concentration and flux in soil solutions decrease significantly with soil depth because DOM is adsorbed along the soil profile. High molecular weight fractions are preferentially adsorbed when compared with low molecular weight components (Gu et al., 1995). The presence of aromatic rings, carboxylic acids, N- and S-containing groups, and amino acid residues in organic molecules increases the adsorption capacity (McKnight et al., 1992). Adsorption involves the free surfaces of colloidal minerals and the presence of organic matter which has already been adsorbed further reduces DOM adsorption (Kalbitz et al., 2000).

Anions in soil solutions, such as sulphate and phosphate, compete with DOM for adsorption sites (Tipping, 1981). Kaiser & Zech (1997) and Beck et al. (1999) confirmed the role of phosphate in DOM removal from adsorption sites: this behaviour is also observed when the phosphate concentration is lower than the concentrations of other anions. Competition between sulphate and DOM for adsorption sites is evident when the sulphate concentration is higher than 10 mM (Kaiser & Zech, 1998).

Polyvalent (Al<sup>3+</sup>, Fe<sup>3+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>) or monovalent (Na<sup>+</sup> e K<sup>+</sup>) cation activity affects the solubility of organic matter (Baham & Sposito, 1994). Chemical reactions between anionic functional groups of organic molecules and solution cations can reduce the surface charge density, alter the structural conformation of the adsorbed species, and consequently reduce solubility. At high concentrations of ions in solution, these processes increase and the solubility of organic matter is reduced by flocculation (Tipping & Woof, 1990).

Various environmental factors influence DOM concentrations and fluxes in soils. Temperature is always a factor regulating DOM microbial production (Mulholland et al., 1990).

One of the most consistent findings in both field and laboratory studies is that DOM concentrations increase following rewetting after dry periods (Lundquist et al., 1999; Tipping et al., 1999; Zsolnay et al., 1999). It is likely that reduced rates of decomposition in dry soils cause microbial products to accumulate. This, together with cell death and lysis, can contribute to high DOM concentrations in the soil leachate after dry periods.

The significant effect of precipitation and water fluxes on DOM is the DOM release at the beginning of large rainfall events. Storm events can alter DOM concentration and flux: high pore water velocity leads to low contact times between the soil solution and the solid matrix and creates chemical and physical nonequilibrium conditions. These conditions increase the DOM concentration in the soil solution leaving the soil poor in organic matter.

Land use changes, such as afforestation, liming, and fertilization, converting forests into arable sites, and other management activities influence DOM dynamics by i) changing the input of organic matter, ii) changing the substrate quality and iii) altering the rates, extent, and pathways of microbial degradation and the synthesis of organic matter (Cronan et al., 1992).

The understanding of the dynamics and fluxes of DOM in soils is important in limiting the loss of organic matter from the soil, improving agronomic practices, and reducing the environmental impact of substances adsorbed on the DOM, such as agrochemicals.

### 5.1 The effect of DOM on the fate of herbicides

The water solubility of herbicides is one of the most important physical properties controlling the transport and fate of chemicals in aquatic systems (Chiou et al., 1986). The formation of soluble complexes between agrochemicals and DOM can be considered responsible for the transport of pollutants towards water bodies. Previous studies have indicated that low concentrations of dissolved and/or suspended particulate-bound natural organic matter in water can significantly enhance the solubility and stability of many hydrophobic organic compounds, notably DDT and some polychlorobiphenyls (PCBs) (Wershaw et al., 1969; Hassett and Anderson, 1979; Caron et al., 1985).

Chiou et al. (1986) observed the water solubility enhancement of solutes characterized by low water solubility such as DDT, 2,4,5,2',5'-PCB, trichlorobenzene, and lindane, due to their interaction with the dissolved humic and fulvic acids extracted from soil and aquatic sediments. The effectiveness of DOM in enhancing solute solubility appears to be largely controlled by DOM molecular size and polarity.

In the presence of soil, contradictory results have been obtained in studies concerning the effect of DOM on the behaviour of cationic or positively ionisable pesticides in soil and waters probably owing to different experimental conditions (Pennington et al., 1991; Barriuso et al., 1992; Klaus et al., 1998; Seol & Lee, 2000).

The nature of DOM (exogenous or endogenous) influences the adsorption and desorption of dimefuron, atrazine and carbetamine (Barriuso et al., 1992). The authors observed that DOM chemico-physical properties, like organic carbon content, pH, and conductivity, strongly affect herbicide adsorption. Moreover, different DOM additions to soils (pretreatment with DOM solution before herbicide adsorption or preincubation of DOM solution with herbicide before soil addition) influences adsorption as a function of herbicide solubility. Increased adsorption of less soluble atrazine and dimefuron, after soil pretreatment with DOM solution, can be explained by an increase in soil adsorption capacity related to the increase of soil C content via adsorption of some organic compounds from DOM solutions. The fate of the highly soluble carbetamide is different: its adsorption decrease can be explained by the coverage of soil hydrophilic sites by DOM organic compounds adsorbed during the preincubation.

Pennington et al. (1991) observed an opposite behaviour of the DOM: no interactions between the DOM extracted from different soils and the herbicides bromacil, metribuzin, alachlor, were observed. Diquat and paraquat are weakly adsorbed on DOM and their adsorption onto soils is not affected by the presence of soluble organic matter.

Despite the negative charge of negatively ionisable pesticides, which constrains them in the soil liquid phase and subsequently, in water courses, only a few studies on their behaviour in soil in the presence of DOM have been conducted (Spark & Swift, 2002; Said-Pullicino et al. 2004).

Although the interactions of pesticides with DOM are affected by the ionic strength of the solutions, DOM is often used in laboratory trials, after the removal of salts, i.e. as a purified organic fraction, or further fractionated in humic and fulvic acids (Spark & Swift, 2002; Chiou et al., 1986). Metals bound to DOM constituents or contained in free form are lost during the purification procedure, and rarely purified DOM has been studied as a function of both the ionic strength and saline composition (Carter & Suffet, 1982).

### **5.2 Case study: The fate of cyhalofop herbicide in soils treated with DOM from composts**

Cyhalofop-butyl (butyl(R)-2-[4-(4-cyano-2-fluorophenoxy)phenoxy]propionate, Clincher™), is an acetyl CoA carboxylase inhibitor for post-emergence control of barnyard grass (*Echinochloa* spp) and silver top (*Lepthochloa fusca*) in rice (Buendia et al., 1998; APVMA, 2005). The esters of aryloxyphenoxyalkanoic acids act as pro-herbicides. The formulation as esters facilitate the uptake through the plant cuticle and, once inside the plant, are transformed within a few hours into their acidic form, i.e. the active herbicide (Hendly et al., 1985; Ferreira et al., 1995). In soils, cyhalofop-butyl is quickly transformed into its more soluble negatively ionisable acidic form (Jackson & Douglas, 1999).

The potential for contamination of water bodies is high in areas where rice is cultivated in flooded conditions (Celis et al., 1998; Charizopoulos & Papadopoulou, 1999; Cerejeira et al., 2000; Miao et al., 2003). Agrochemicals applied to aquatic environments such as paddy-fields are matter of concern due to their potential leaching (Boesten & van der Linden, 1991; Müller et al., 2007) and persistence in soil and waters (Braschi et al., 2003).

The addition of organic amendments to the soil is an agricultural practice that is considered to potentially affect the fate of pesticides in soil (Cox et al., 2001; Hesketh et al., 2001), by introducing a remarkable amount of exogenous soluble organic matter. The extent to which exogenous DOM is involved in transportation through the soil is yet to be understood.

The effect of exogenous DOM from two composts on the behaviour of cyhalofop-butyl (CB) and cyhalofop-acid (CA) (Figure 2) was studied in two different soils (a paddy-field sediment, and a forest soil, Table 3) by means of solubility tests, determination of adsorption-desorption isotherms in soils, leaching experiments on soil columns (for experimental details, see Blasioli et al., 2008). To study the effect of the saline component on herbicide behaviour in soils, DOMs were used without any desalting treatment or pH modification.

Cyhalofop-butyl degradation is slow in the paddy-field sediment and leads to the cyhalofop-acid formation; in the forest soil, the degradation is faster and three byproducts were detected (cyhalofop-acid, -amide, and -diacid, Figure 2). The degradation is mediated by microorganisms as confirmed by the cyhalofop-butyl stability in autoclaved soils.

The water solubility of cyhalofop-butyl is unchanged in DOM solution at pH 6.0. This probably results from the highly hydrophilicity of these DOMs in contrast with the completely hydrophobic character of CB molecule. On the contrary, the solubility of CA doubles suggesting interaction with the DOMs. Since at working pH (about 6.0) cyhalofop-

Soil	pH		TOC <sup>a</sup> (g kg <sup>-1</sup> )	CEC <sup>b</sup> (cmol <sub>(+)</sub> kg <sup>-1</sup> )
	H <sub>2</sub> O	CaCl <sub>2</sub>		
<b>Paddy-field sediment</b>	6.00	5.50	14.0	2.00
Forest soil	7.10	6.80	73.0	9.90

Table 3. Summary of the characteristics of investigated soils. <sup>a</sup> TOC: Total Organic Carbon; <sup>b</sup> CEC: Cationic Exchange Capacity (modified from Blasioli et al., 2008).

acid, characterized by a pK<sub>a</sub> of 3.8 (APVMA, 2005), mostly exists in anionic form, a molecular interaction, responsible for this increase in solubility, must occur despite the repulsion between DOM and CA negative charges. Similarly to water and cation bridgings formed between the carboxylate groups of humic substances and the soil phases in the presence of base metals (Sposito, 1984), polar and/or ionic interactions between metal cations-rich DOM and CA anionic moiety may be assumed to be responsible for the increase of CA solubility.

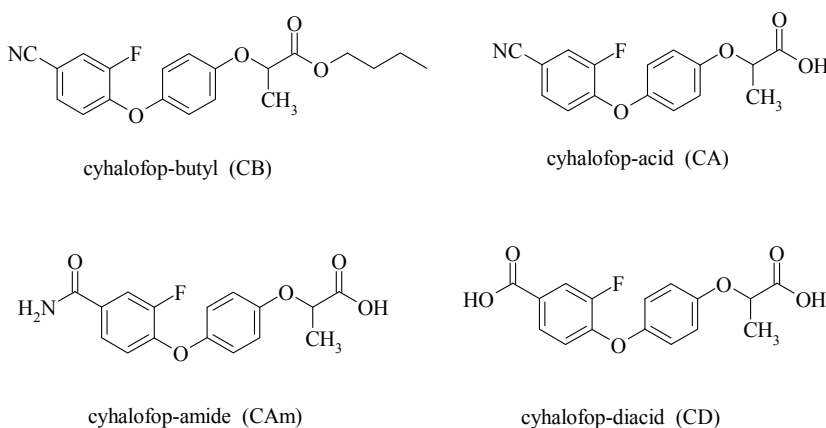


Fig. 2. Structure of cyhalofop-butyl and its byproducts.

The adsorption of cyhalofop-butyl and cyhalofop-acid is higher on the forest soil than on the sediment (Table 4). The pretreatment of soils with DOM solutions significantly decreases the cyhalofop-butyl adsorption but increases that of the acid. Since the DOM does not interact with the cyhalofop-butyl, the adsorption decrease may be due to the occupation by the DOM of soil sites available for the pro-herbicide.

The adsorption of acid is reversible on the paddy-field sediment but not reversible on the forest soil before and after soil pretreatment with DOM solutions. Reversible adsorption can be explained by two mechanisms: *i*) DOM which was previously adsorbed on soil surfaces increases the number of organic sites available to interact with CA by polar/ionic mechanisms; *ii*) the addition of base cations increases the base metal saturation degree of the sediment, hence linking CA carboxylate moiety to a higher extent via cation and water bridges (Sposito, 1984).

On the forest soil, the amount of adsorption sites available for hydrophobic interaction with CA does not vary as a consequence of DOM adsorption on the soil. This is reasonably supported by the very high content of organic matter in forest soil (TOC 73.0 g kg<sup>-1</sup>, Table 3).

Sample	Cyhalofop-butyl		Cyhalofop-acid	
		$K_d$ $L\ kg^{-1}$		$K_{Fads}$ $\mu g^{(1-1/n)} mL^{1/n} g^{-1}$
Paddy-field sediment		1.30		0.52
Paddy-field sediment + DOM <sub>A</sub>	+	n.a.		4.70
Paddy-field sediment + DOM <sub>M</sub>	+	n.a.		2.60
Forest soil		3.34		3.00
Forest soil + DOM <sub>A</sub>		0.85		4.90
Forest soil + DOM <sub>M</sub>		0.61		3.50

Table 4. Distribution coefficient of cyhalofop-butyl and Freundlich constants for cyhalofop-acid adsorbed in soils. n.a.: not available because no adsorption was observed (modified from Blasioli et al., 2008). DOM<sub>A</sub> and DOM<sub>M</sub> extracted from compost A (blend of winery byproducts) and M (blend of municipal solid waste), respectively.

The increases of the adsorption extent after pretreatment of forest soil with DOMs may be due to the ionic content of DOM solutions whose cationic component, complexing the negatively charged groups, lowers the repulsion between the negative charges and hence favours hydrophobic interactions of both soil organic matter and CA.

Adsorption data interpretation has been confirmed by CA leaching experiments on soil columns (Figure 3). The leaching of column with DOM solutions reduces the mobility of cyhalofop-acid in both soils. In fact, on the paddy-field sediment, which is poor in organic matter, the increase in base metal saturation degree due to DOM addition, promotes cation and water bridging formation with the carboxylate CA group. On the forest soil, which is rich in organic matter, the metals contained in the DOM, decrease the electrostatic repulsion between the soil organic matter and the carboxylate groups of the cyhalofop in acid, amide, and diacid forms, by reducing their mobility along the soil profile.

Further confirmation for the adsorption data was obtained by eluting the soil columns with  $K^+$  and  $Ca^{2+}$  solutions (the most representative monovalent and divalent cations found in DOM<sub>M</sub> solution). In both soils, the  $K^+$  ion reduces the mobility of cyhalofop-acid whereas the  $Ca^{2+}$  ion decreases the mobility in the paddy-field sediment but not in the forest soil. The difference in the binding activity of the two cations in the adsorbed form towards the carboxylates can be explained. In fact, while in adsorbed form  $K^+$  may give rise to a cation bridge with carboxylates due to the formation of an inner-sphere complex,  $Ca^{2+}$  forms a water bridge, a weaker outer-sphere complex mediated by water molecules (Sposito, 1984; Theng, 1982). The different strength between the K- and Ca-complexes may be responsible for the best CA retention in soils eluted with K ions in comparison with Ca ions.

In conclusion, the saline component of compost extracts seems to account to a large extent for the increased adsorption of the anionic herbicide cyhalofop-acid in both paddy-field and forest soils, generating highly reversible complexes with the former and non-reversible complexes with the latter, both involving the CA carboxylate group.

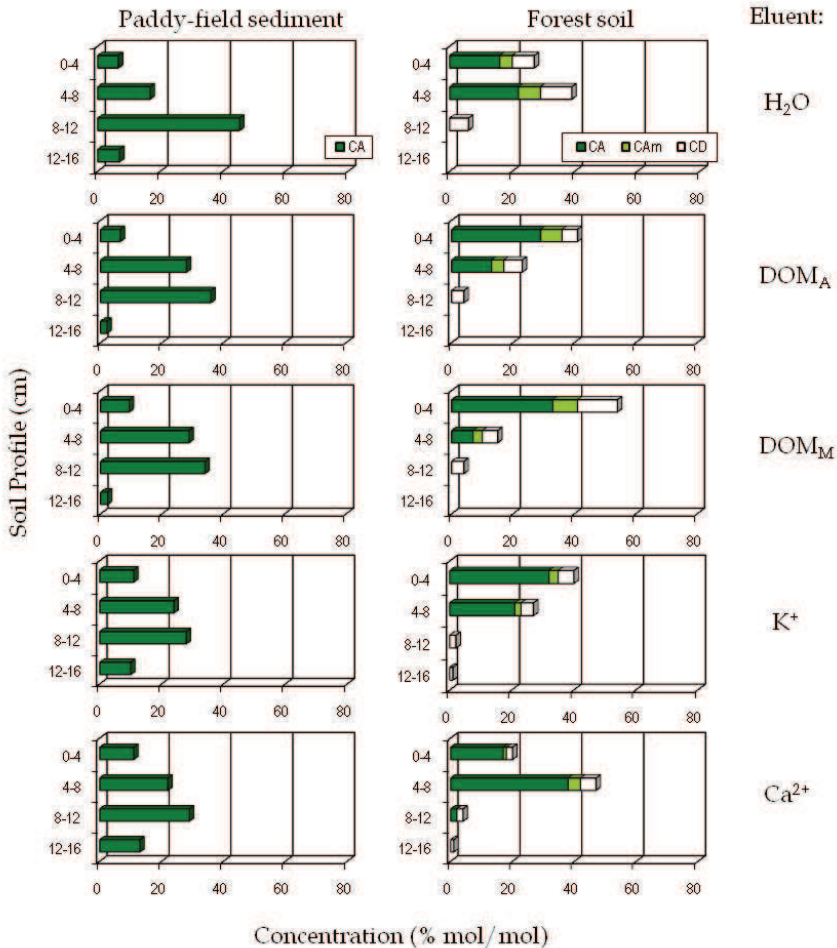


Fig. 3. Mobility of cyhalofop-acid and byproducts along the paddy-field sediment and forest soil column profiles leached with exogenous dissolved organic matter ( $\text{DOM}_A$  or  $\text{DOM}_M$ ) or metal ( $\text{K}^+$  or  $\text{Ca}^{2+}$ ) solutions (mean of two replicates) (modified from Blasioli et al., 2008).

## 6. Conclusions

The prediction of the movement and the fate of herbicides in soils represents an important strategy in limiting their environmental impact. The chemo-physical properties of herbicides affect their behaviour in soil and regulate their interaction mechanisms with organic and inorganic soil phases. Among these, dissolved organic matter plays an important role: DOM influences the mobility of herbicides by complex interactions that can facilitate or reduce the movement of chemicals along the soil profile.

The knowledge of soil phase characteristics and the mechanisms involved in herbicide transformation can help to understand the fate of herbicides in soil.



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## **Herbicides and Environment**

Edited by Dr Andreas Kortekamp

ISBN 978-953-307-476-4

Hard cover, 746 pages

**Publisher** InTech

**Published online** 08, January, 2011

**Published in print edition** January, 2011

Herbicides are much more than just weed killers. They may exhibit beneficial or adverse effects on other organisms. Given their toxicological, environmental but also agricultural relevance, herbicides are an interesting field of activity not only for scientists working in the field of agriculture. It seems that the investigation of herbicide-induced effects on weeds, crop plants, ecosystems, microorganisms, and higher organism requires a multidisciplinary approach. Some important aspects regarding the multisided impacts of herbicides on the living world are highlighted in this book. I am sure that the readers will find a lot of helpful information, even if they are only slightly interested in the topic.

### **How to reference**

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Ilaria Braschi, Carlo Emanuele Gessa and Sonia Blasioli (2011). The Fate of Herbicides in Soil, *Herbicides and Environment*, Dr Andreas Kortekamp (Ed.), ISBN: 978-953-307-476-4, InTech, Available from: <http://www.intechopen.com/books/herbicides-and-environment/the-fate-of-herbicides-in-soil>

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