Fate of Pesticides in Soils: Toward an Integrated Approach of Influential Factors

Véronique Chaplain[1], Laure Mamy[1], Laure Vieublé-Gonod[2],
Christian Mougin[1], Pierre Benoit[2], Enrique Barriuso[2] and Sylvie Nélieu[1]
[1]INRA, UR 251 PESSAC, Versailles,
[2]INRA-AgroParisTech, UMR 1091 EGC, Grignon,
France

1. Introduction

Despite constraining legislation and increasing efficiency of pesticides (with a decrease in the applied amounts), their use still cause a contamination of environment (air, soil and water). To conciliate agricultural and environmental interests, a better understanding of the fate of pesticides is needed, in particular because it will determine the exposure and consequently the impact of pesticides on the target and non-target organisms. This goal requires new efforts of research at different scales (from molecular to field scale). Following application, most of the pesticides reach the soil either after direct application or after foliage wash-off. As a major interface between other environmental compartments, the soil plays a preponderant buffering role in the fate of pesticides. Apart volatilization, the main processes that control the fate of pesticides in soils are retention on soil particles and degradation (biotic and abiotic). These coupled bio-physico-chemical processes can lead to a transitory or permanent accumulation of pesticides in soils or, on the contrary, to their elimination from the environment. They determine the pesticide concentration in the soil solution, and have a large influence on pesticide transfer toward ground or surface waters and on their ecotoxicological impacts on soil organisms as well. The main difficulties in studying and predicting the retention and degradation of pesticides in soils are the diversity of chemical structures and reactivities of pesticides, the high diversity of soils and their heterogeneous composition and structure. In addition, the pedoclimatic conditions, in particular soil temperature and water content, have a strong influence on retention and degradation because of their effect on soil biological, chemical and physical properties. Therefore, the objective of this chapter is to provide an overview of the factors involved in the retention and degradation of pesticides in soils and to discuss and clarify the needs of new integrated approach. In particular, this work will examine (i) the pertinent scales (among elementary constituents, aggregates and mesoscopic scales) for both retention and degradation studies, (ii) the integrative properties that should be considered, such as hydrophobicity of the organo-clay granulometric fraction or soil structure, and (iii) the primordial role of water.

2. Retention

2.1 Definitions
The retention of pesticides in soils is mainly due to the adsorption, which is the passage of a solute from an aqueous phase to the surface of a solid adsorbent (Calvet, 1989). The solid

adsorbents are the different soil constituents. According to the properties of pesticides and adsorbents, several adsorption mechanisms are possible: hydrogen bindings, ion exchanges, interactions with metallic cations, polar interactions, charge transfers, London-Van der Waals dispersion forces and hydrophobic effects (Calvet et al., 2005). As the soil constituents contain polar and ionisable groups, the adsorption of pesticides possessing polar and non polar groups can involve several of these mechanisms. The reverse process of adsorption is desorption. In general, the desorption is inversely related to adsorption, being small when adsorption is great, and conversely (Mamy & Barriuso, 2007). For example, the adsorption of atrazine is fully reversible (Celis et al., 1998); on the contrary that of glyphosate is not reversible and hysteresis is observed (Mamy & Barriuso, 2007). The hysteresis can be due to irreversible adsorption, physical entrapment in organo-mineral aggregates or degradation.

2.2 Methods of measurement

Batch experiments. Most of the time, the retention of pesticides is measured with soil suspensions, known as batch experiments, according to the OECD 106 guideline (OECD, 2000a). A volume (generally 10 mL) of an aqueous solution of pesticide is added to a mass of dry sieved soil (generally 2 g) in glass centrifuge tubes. Soil suspensions are shaken mechanically for 24 hours in darkness and then centrifuged. The duration of 24 hours corresponds to the time needed to reach equilibrium between the adsorbed pesticide and the pesticide in solution. The degradation of the pesticide or the adsorption of the pesticide on the surface of the flask used for the experiment has to be determined (Calvet, 1989). The amounts of adsorbed pesticide in the soil are calculated as the difference between initial pesticide concentration in solution and centrifuged supernatant concentration. This experiment is done at several initial pesticide concentrations to determine the adsorption isotherm of the pesticide (adsorbed amounts as a function of the equilibrium concentration of pesticide). In general, the smaller the concentration, the greater the adsorbed amount per unit mass soil. From this isotherm, distribution coefficients between soil and soil solution can be determined according to the Freundlich (Kf) model (1):

$$Kf = Qs \ / \ Ce^{nf} \tag{1}$$

where Qs (mg kg^{-1}) is amount of adsorbed herbicide in soil at equilibrium concentration, Ce (mg L^{-1}) is pesticide concentration in supernatant solution, and nf is an empirical coefficient. When $nf = 1$, the isotherm is linear and $Kf = Kd$ (L kg^{-1}). As organic carbon is a major adsorbent for pesticides (see 2.3.2.1), the Koc (L kg^{-1}) (2) coefficient is often calculated as:

$$Koc = (Kd \times 100) \ / \ Corg \tag{2}$$

where $Corg$ is the percentage of organic carbon content in soil.
For a given pesticide, the Koc is generally less variable than the Kd among different soils (Calvet, 1989). However, the intensive shaking of soil-pesticide solution leads to dispersion of the soil structure, resulting in a higher availability of sorption sites. Therefore batch overestimates the sorption of pesticides (Walker & Jurado-Exposito, 1998).
Centrifugation. The soil sample is prepared at realistic soil moisture, treated with the pesticide, incubated, then centrifuged to collect the soil solution which is directly analysed for pesticide concentration (Benoit et al., 2007; Walker & Jurado-Exposito, 1998).
Filters. Gaillardon & Dur (1995) developed an original method using remoulded soil samples that are placed in Petri dishes to give a 3-4 mm thick soil layer at controlled water

content. The soil solution is sampled with glass microfibre filters laid on the soil surface. The volume of the soil solution and the dissolved pesticide retained in the filter are determined. This method could be adapted to undisturbed soil samples.

Soil columns. The soil columns allow the study of retention in dynamic conditions. The column is filled with disturbed (sieved or small aggregates) or undisturbed soil, a solution of pesticide is applied at the top of the column then water flow is imposed through rainfall simulation or pressure head control (Pot et al., 2005; 2011). Sorption coefficients can be estimated by inverse modelling of the elution curves and retardation factor calculation (Lennartz, 1999). Column experiments allow the possibility to determine the vertical distribution of the pesticide residues in the soil core if recovery in the leachates is incomplete (Benoit et al., 2000; Vincent et al., 2007). In a recent study, Vereecken et al. (2011) analysed the relationships between Koc derived from column data with more classical batch experimental data obtained on the same soils. The authors concluded that such relationships depended on pore water velocity and on the saturation status (saturated *vs* unsaturated) and packing status (disturbed *vs* undisturbed) of the soil column.

Lysimeters. A lysimeter consists of an undisturbed soil block or cylinder, embedded in an inert container with a bottom permeable to drainage water or leachate. An outstanding feature of lysimeters is the capability to monitor mass fluxes of water and chemicals under field climatic conditions and representative crop practices (Saison et al., 2008). The distribution of the chemical and of its metabolites in the soil along with their transformation rates can also be determined. Compared to laboratory experiments, outdoor lysimeter studies are closer to field environmental conditions, there is no significant disturbance of the soil structure, but the major limitation is the fact that certain variable experimental conditions such as environmental/climatic parameters are not controlled (OECD, 2000b).

2.3 Factors controlling the retention of pesticides in soils
2.3.1 Physico-chemical properties of pesticides

Surface, volume, and branching. In general, the adsorption of pesticides increases with the volume and with the degree of branching which is correlated to the surface area (Mamy & Barriuso, 2005; Sabljic et al., 1995). Indeed, the molecular volume is related to water solubility (see hydrophilic/hydrophobic balance) (Calvet, 1989), and the degree of branching encodes the intermolecular accessibility (Kier & Hall, 2000).

Electronic structure. The nature of atoms and of functional groups determines the electronic structure of the pesticides (therefore their permanent dipole moment and polarizability) that governs the type of interactions of pesticide with soils (donor-acceptor electron, hydrogen bonds) (Calvet, 1989). The different substitutions and their spatial arrangement in the molecule have an effect on the adsorption by influencing the reactivity of functional groups (carbonyl oxygen, amide nitrogen) participating in these bond interactions (Liu et al., 2000).

Ionization. It determines the charge of the pesticide and depends on its electronic structure. Strong bases always occur in cationic form in soils, but the ionization of weak bases and weak acids depends on the pH of the soil and on pKa or pKb values of molecules (Calvet, 1989). In general, the sorption of cations is strong on negatively charged surfaces like clays, oxides, hydroxides and humic substances. On the contrary, anions are not adsorbed on these surfaces, but their sorption is high in soils with positive charges, like tropical soils. For example, glyphosate has four pKa so that its sorption increases when the soil pH decreases because the number of negative charges of this herbicide decreases.

Hydrophilic/hydrophobic balance. The hydrophilicity of pesticides is defined by their water solubility and the hydrophobicity by their octanol/water partition coefficient. In general, the adsorption of pesticides decreases when their water solubility increases because of their high affinity for the water phase, and conversely, the adsorption increases with the hydrophobicity of pesticides. However, it also depends on the hydrophilic/hydrophobic balance of the soil adsorbents. The adsorption of polar compounds does not always decreases with increasing water solubility (Calvet, 1989). For example, glyphosate, a polar herbicide, is highly soluble in water (12 g L^{-1}) but is strongly sorbed to soils (Mamy & Barriuso, 2005). Indeed, the sorption of ionisable molecules and molecules with phospho-groups like glyphosate involve high-energy binding adsorption phenomena (ionic and coordination bindings, complex formation with metals in solution or at the solid–liquid interphase) that overbalance the effects of high solubility (Tao & Lu, 1999).

2.3.2 Soil properties

2.3.2.1 Elementary properties (minerals, organic matter, pH)

Minerals. The mineral adsorbents involved in the adsorption of pesticides are clays (as silicate minerals), oxides and hydroxides (Calvet, 1989). Their surfaces are mainly hydrophilic because of hydroxyl groups and exchangeable cations. The adsorption of pesticides on clay minerals is likely to occur on external surfaces of clay particles rather than in interlamellar space and increases with the specific surface of clays (Barriuso et al., 1994). Oxides and hydroxides are frequently associated to clays, they have a high surface activity and their charge depends on the soil pH (Calvet, 1989). For example, the adsorption of glyphosate increases as follows: kaolinite < illite < montmorillonite < nontronite (Mc Connell & Hossner, 1985). The adsorption of glyphosate on iron and aluminium oxides and hydroxides is high at intermediate pH and driven by ionic bindings between the positive surface sites of minerals and the negative acid groups of glyphosate (Morillo et al., 2000). However, sorption is much lower at very acid or very alkaline pH because oxides will bear the same charge as glyphosate.

Organic matter. Soil organic matter originates from crop residues, microbial biomass and organic amendments. It has very heterogeneous composition and contains both hydrophilic and hydrophobic groups (Calvet et al., 2005). Even if organic matter only represents few percents of the total dried material in soil, it is a major sorbent of pesticides in soil (Calvet, 1989). This is attributed to its high chemical reactivity towards both mineral surfaces and organic molecules, allowing various types of interaction with pesticides. The sorption capacities of organic matter are not only controlled by their chemical composition, but also by their size, due to a greater number of sorptive sites related to a greater surface area with decreasing particle-size (Benoit et al., 2008). In general, the adsorption of pesticides increases with organic matter, except for ionic molecules.

Soil pH. The soil pH plays an important role in particular for the adsorption of ionic pesticides like glyphosate or sulcotrione (Calvet, 1989; Mamy & Barriuso, 2005). Depending on the charge of the pesticide, the adsorption will increase (or decrease) with pH. For example, the retention of glyphosate increases when the soil pH decreases because the number of negative charges of the molecule decreases, allowing the adsorption on negatively charged adsorbents like clay or organic matter.

2.3.2.2 Soil structure

The soil structure is characterized by the bulk density and the pore geometry which depend on agricultural practices and on the climate. In addition, the bulk density depends on the size of the soil sample (from aggregate to macroscopic scale) due to the spatial variability of the soil structure (Alletto et al., 2010a). Pesticide movement through aggregated soils is mainly controlled by kinetic sorption and diffusion (Beulke et al., 2004). In static conditions, the rate of pesticide adsorption decreases when the density of soil aggregates increases (Chaplain et al., 2008). In dynamic conditions, retention depends on transport parameters such as pore water velocity and residence time (Pot et al., 2005; 2011). Compared to tilled soils, the no tilled or grassland soils are characterized by the presence of biopores (due to earthworm burrows, roots…) and high content of organic matter in the surface layers. The retention of pesticides is therefore generally higher in these soils (Benoit et al., 2000; Larsbo et al., 2009). However, the increase in retention can be counter-balanced by increased preferential transport because no tillage leads to enhanced macropore connectivity (Larsbo et al., 2009).

2.3.3 Effect of environmental conditions (water content, temperature)

Water content. The soil water content defines the specific exchange surface between solid and liquid phases. The adsorption of pesticides increases with water content as it facilitates pesticide diffusion to sorption sites. As water content increases, the organic matter also becomes more hydrophilic with greater sorption potential for hydrophilic pesticides (Roy et al., 2000). For hydrophobic pesticides like trifluralin, the adsorption decreases when the soil water content increases because the hydration of the surfaces of adsorbents decreases the accessibility to adsorption sites (Swann & Behrens, 1972). Low soil moisture content might also favour access to the hydrophobic regions of humus by generating more hydrophobic surfaces, thereby increasing the sorption of hydrophobic substances (Roy et al., 2000).

Temperature. In general, the adsorption of pesticides decreases when the temperature increases (Ten Hulscher & Cornelissen, 1996). However, fast sorption should be differentiated from slow sorption: the fast sorption increases with decreasing temperature, but the slow sorption is more rapid at higher temperature. This could explain why for some compounds, overall sorption with short equilibration times is nearly independent of temperature. The slow sorption is generally due to diffusion of the pesticide through the organic matter and increasing temperature decreases the density therefore increases the diffusion (Ten Hulscher & Cornelissen, 1996). For some pesticides that exhibit decreasing solubility at higher temperatures, an increase in the sorption with temperatures can be observed (Chiou et al., 1979, as cited in Ten Hulscher & Cornelissen, 1996).

2.3.4 Spatio-temporal variability of retention

Spatial variability. The retention of pesticides varies laterally and vertically. For example, at the scale of one watershed, the variation coefficients of the Koc of several pesticides in the soil surface can reach 30%. It seems mainly due to the variation of organic carbon content (Coquet & Barriuso, 2002). But, the variability of pesticides adsorption is high even at smaller scales (cm to m) (Mermoud et al., 2008, Vieublé-Gonod et al., 2009). The adsorption of pesticides also varies with soil depth: in general, the adsorption decreases because of a decrease in the organic carbon content (Mamy & Barriuso, 2005).

Temporal variability. The retention of pesticides is affected by their residence time in soil because of diffusion into soil micropores, physical entrapment or degradation (Koskinen et al., 2001). In the long term, the interactions responsible for retention evolve to the formation of pesticides non-extractable residues (Barriuso et al., 2008). Non-extractable (bound) residues are pesticides in soils which persist in the form of the parent substance or its metabolite(s) after extraction (Fürh et al., 1998, as cited in Barriuso et al., 2008). A large increase in retention with time is generally observed for weakly adsorbed herbicides, but for strongly adsorbed herbicides, adsorption decreases or remains stable (Mamy & Barriuso, 2007).

3. Degradation

3.1 Biodegradation
3.1.1 Definitions

Metabolism of pesticides. The metabolism of pesticides in living beings involves numerous enzymatic reactions grouped in three phases (Bollag & Liu, 1990; Mougin, 2002). Phase 1, probably the most important one, includes functionalization reactions (oxidation, reduction, hydrolysis) of the parent compound. By the introduction of additional functional groups such as OH, NH_2, SH and COOH, these processes often result in the formation of metabolites with modified physiological and biological properties, and a predisposition for further metabolism in the secondary phase. Phase 2 is a synthetic process known as conjugation that results in the formation of final metabolites by linkage of the activated metabolite with cell constituents. These metabolites are distributed and sequestered by the organisms, or excreted. Phase 3 involves synthetic reactions leading to the oligomerization of several units of the parent compound, or secondary conjugation of the parent compound with cellular components of the cells. They contribute to the formation of high-molecular weight compounds or bound compounds, which are incorporated and stabilized within the cells. In moving from their initial state to phase 2 or 3, metabolites become generally more hydrophilic, except in the case of insoluble polymers. Their initial mobility is also reduced, as well as their toxic or hazardous power.

Key actors responsible of pesticide metabolism. The degradation of pesticide through microbial metabolic processes is considered to be the primary mechanism of biological transformation. The different groups of microorganisms, mainly the prokaryotic bacteria, actinomycetes and eukaryotic fungi, can mediate an almost infinite number of biochemical transformations. The most numerous organisms in soil are bacteria, whereas fungi form the largest biomass. They are involved in other numerous functions such as mineralization and humification of organic matter, biogeochemical cycles, production of toxins and compounds of interest (antibiotics). Bacteria are the main biodegraders in soils. They are present in all soils with a competitive pH near neutrality. Despite some characteristics in common with bacteria, actinomycetes are similar to fungi. They are more tolerant to alkaline and acidic soil pH and low moisture content than bacteria.

Processes involved in the biotransformation of pesticides. The processes responsible of the biodegradation of pesticides include biodegradation, cometabolism and synthesis.

During biodegradation, one or several interacting organisms metabolize the pesticide into inorganic components (like CO_2). The organisms obtain their requirements for growth and energy by mineralizing the molecule. If microorganisms do not possess all the enzymatic equipment to mineralize pesticides, metabolites are excreted in soil and can be mineralized by other microorganisms.

Pesticide metabolism in the environment is also governed by cometabolism in which organisms grow at the expense of a cosubstrate to transform the pesticide without deriving any nutrient or energy for growth from the process. Cometabolism is a partial and fortuitous metabolism and enzymes involved in the initial reaction lack substrate specificity. Generally, it results only in minor modifications of the structure of the pesticide, but these modifications could greatly influence pollutant bioavailability and mobility in soil. Different organisms (mainly fungi) can transform a molecule by sequential attacks, or can use cometabolic products of one organism as a growth substrate. In addition, intermediate products with their own bio-physico-chemical properties can accumulate, thus causing some adverse effects on the environment. The metabolites are generally less toxic than the pesticides, but they can be more toxic in some cases (Tixier et al., 2002).

Synthesis includes conjugation and oligomerization. Pesticides are transformed into compounds with chemical structures more complex than those of the parent compounds. During conjugation, a pesticide (or one of its transformation products) is linked to hydrophilic endogenous substrates, resulting in the formation of methylated, acetylated, or alkylated compounds, glycosides, or amino acid conjugates. These compounds can be excreted from the living cells, or stored. During oligomerization, a pesticide combines with itself, or with other xenobiotic residues (proteins, soil organic residues). Consequently, they give high-molecular weight compounds, which are stable and often incorporated into cellular components (cell walls…) or soil constituents (soil organic matter). This biochemical process not only affects the activity and the biodegradability of a compound in limiting its bioavailability, but also raises concern about the environmental impact of the bound residues (Barriuso et al., 2008; Bollag & Liu, 1990).

3.1.2 Methods of measurement

Pure liquid cultures. Pesticide metabolism can be studied with pure liquid cultures supplemented with fungal or bacterial inocula. These cultures are potent tools to precise the transformation pathways of pesticides and the relevant metabolites. For example, white-rot basidiomycetes have been extensively considered because of their high potential for xenobiotics transformation. These filamentous fungi degrade pesticides using two types of enzymatic systems: intracellular (cytochromes P450) and exocellular (lignin-degrading system mainly consisting in peroxidases and laccases). Each of these systems could also be induced or inhibited by pesticides, thus able to modulate their metabolism.

Soil and inoculum. Studies can be performed in soils favouring microbial development and activity. Some experiments involved bacteria as an inoculum to remove pesticide residues from contaminated soils in laboratory conditions (Duquenne et al., 1996) or *in situ* (Qureshi et al., 2009). In some cases, carriers are developed to ensure fungal growth in the spiked soil. Lignocellulosic materials, that provide also nutrients and easily available carbon for the organisms, have been often retained. Nevertheless, fungal growth or activity are rarely assessed using biological descriptors in biotransformation experiments.

Soil incubation (disturbed or undisturbed soils). The degradation of pesticides is often studied using soil incubation. Soil samples are treated with the pesticide and incubated in the dark under controlled laboratory conditions (at constant temperature and soil moisture). After appropriate time intervals, soil samples are extracted and analysed for the parent substance and for metabolites. Volatile products are also collected for analysis. Using ^{13}C or ^{14}C-

labelled material, the mineralization rates of the pesticide (allowing the quantification of biodegradation) can be measured by trapping evolved $^{13}CO_2$ or $^{14}CO_2$, and a mass balance, including the formation of soil bound residues, can be established (OECD, 2002). From the degradation kinetics, the half-lives (DT50) of pesticides are determined. This method can use either disturbed soil samples (sieved) or undisturbed soil samples such as aggregates or cores (Benoit et al., 2000; Mamy et al., 2011; Monard et al., 2010; Vieublé-Gonod et al., 2009).

Field studies. In field conditions, soil temperature and moisture are highly variable with consequences on pesticides degrading microorganisms. Therefore, the measurement of pesticide dissipation in the field is fundamental to complete the data obtained in the laboratory. The pesticide is applied according to the intended use and, at appropriate dates, the soil is sampled and analysed for the pesticide and its metabolites. The DT50 can then be determined.

3.1.3 Factors controlling the degradation of pesticides in soils

3.1.3.1 Physico-chemical properties of pesticides

There is no clear relationship between the chemical properties of pesticides and their rates of degradation because several phenomena are simultaneously involved in the degradation and because of the high variety of structures of pesticides (Calvet et al., 2005). Nevertheless, some atoms (halogens, and chlorine in particular) are known to be toxic to microorganisms (therefore a decrease of biodegradation is observed), but there is no general rule (Naumann, 2000). For example, there is almost no biodegradation of chlordecone (organochlorine insecticide) because of its highly chlorinated cage-like structure that makes chlordecone a poor carbon source for bacteria (George & Claxton, 1988, as cited in Cabidoche et al., 2009).

3.1.3.2 Effect of soil structure on the degradation of pesticides in soils and spatio-temporal variability

Soil structure. The different practices such as soil tillage or organic amendments may affect soil structure by different mechanisms (aggregation of soil particles, creation of pore space) (Mapa et al., 1986), influence the hydraulic properties of the soil and hence pesticide transport through the soil (see 2.3.2.2). When an increase of leaching is observed in conventional tilled soil, this can be attributed to weaker sorption due to lower soil organic carbon content but also to slower microbial degradation (Gish et al., 1995 and Sadeghi et al., 1998 as cited in Alletto et al., 2010b). Tillage also affects soil organic carbon location and sequestration as well as water retention properties. This may lead to different sorption and degradation properties depending on tillage practices (Alletto et al., 2008; Stenrød et al., 2006). In agricultural soils, soil structure is affected by compaction under wheel tracks. Vieublé Gonod et al. (unpublished data) studied the impact of compaction on the fate of isoproturon in soil in laboratory. They did not observe any effect of compaction neither on isoproturon mineralization nor on its availability. The presence of fresh organic matter originating from urban waste compost did not modify the observed results. This was consistent with the results of Mamy et al. (2011) who showed that, in the conditions of the experiment, soil compaction did not modify significantly the degradation of isoproturon, neither the formation rates nor the nature of its metabolites.

Spatial localization of microorganisms. The spatial heterogeneity of microorganisms in heterogeneous soil structure plays an important role in microbial processes and in the persistence of pesticides (Strong et al., 1998). For example, Vieublé-Gonod et al. (2003)

observed that 2,4-D mineralization increased with the size of aggregates (inter classes heterogeneity) but varied also a lot in aggregates of a same size class (intra class heterogeneity). Authors explained this variability by an uneven distribution of the degrading microorganisms at this scale, and to a lesser extent, by an uneven distribution of carbon, necessary for cometabolism. Soil aggregates or small soil cubes enriched in 2,4-D degrading microorganisms were not distributed randomly in soil, but rather grouped into centimetric hot spots (Vieublé-Gonod et al., 2003; 2006). In a simulation, Vieublé-Gonod et al. (2006) showed that if soil cubes having a high potential of mineralization (hot spots of mineralization) were either not in direct contact with the pesticide (within soil clods, not exposed to preferential flow paths) or in direct contact with it (on the periphery of clods), 2,4-D mineralization was differently affected and was equal to 2% and 75% of added C, respectively. Cohen et al. (unpublished data) studied the impact of soil structure on isoproturon mineralization in small columns made of structured or sieved soil sampled in plots amended or not with a co-compost of green waste and sewage sludge or with a municipal solid waste. They showed that soil structure significantly affects isoproturon mineralization only in soil amended with compost (not in the control). But the effect also depended on type of compost. In soil amended with the co-compost of green waste and sewage sludge, isoproturon mineralization was stimulated in structured samples whereas in soil amended with a municipal solid waste compost, opposite results were observed. At a smaller scale, when comparing the mineralization of 2,4-D by intact aggregates to that of crushed ones, Vieublé Gonod et al. (2003) highlighted that disruption of the soil structure by crushing did not affect pesticide mineralization.

Effect of time. Soil structure can protect a fraction of pesticide from biodegradation and this phenomenon is emphasized when pesticides are "aged". Indeed, some works noticed that, over time, xenobiotics may become resistant to biodegradation (*e.g.* Nam et al., 1998) because pollutants may become physically segregated from degrading bacterial species. Hydrophobic pesticides could become inaccessible through their diffusion within the organic matter or micropore network (Shaw et al., 2002). Steinberg et al. (1987) demonstrated that degradation of aged 1,2-dibromomethane by indigenous microorganisms was negligible when compared to rapid mineralization of freshly added compounds and explained it by the entrapment of aged compounds in intraparticle micropores.

3.1.3.3 Effect of environmental conditions (water content, temperature)

Water content. Variations in soil moisture have effects on the diffusion of soluble substrates and on the mobility of microorganisms at lower soil water content, while at higher soil moisture diffusion of oxygen can become restricted, both of which affecting activity of soil microbial communities (Skopp et al., 1990). It is important to consider water content at a given pressure head rather than to compare gravimetric or volumetric water content (Alletto et al., 2006; 2008). Generally, aerobic microbial activity increases with soil water content up to a maximum point before decreasing (Linn & Doran, 1984). For example, Schroll et al. (2006) showed an optimum mineralization for isoproturon, benazolin-ethyl, and glyphosate at a soil water potential of -0.015 MPa, whereas, pesticide mineralization was considerably reduced when soil moisture approximated water holding capacity. Some fungi such as the white-rot *Trametes versicolor* may degrade triazines under low water availability conditions (Bastos & Magan, 2009). Because fungi often degrade pollutants using exocellular enzymes, these enzyme-catalyzed processes should be regulated in soils with respect to moisture for an optimal activity (Baldrian, 2009). Soil moisture affects not only the activity but also the

diversity of soil microbes (Bouseba et al., 2009). For example, fungi have an adaptative advantage with respect to bacteria to water fluctuations. The hyphal/mycelial growth form, present in fungi, facilitates organisms to cross water-poor or nutrient-poor spots (Yuste et al., 2011). As a consequence, fungi can tolerate a broad range of environmental conditions, including moisture content. The reduction of the microorganisms activity at lower soil water content could increase the contact times between the pesticide and the soil components, and so may favour long-term sorption (Cox & Walker, 1999). It could explain why some authors concluded that the amount of bound residues seemed to be inversely proportional to mineralization. These results also explain why pesticide degradation is reduced (with increase in persistence) in areas characterized by elevated temperature and limited rainfall (Bouseba et al., 2009).

Temperature. Alletto et al. (2006) demonstrated that isoproturon mineralization was largely affected by temperature in both surface and subsurface soils but degradation seemed more sensitive to water content variations than temperature ones. Pesticide biodegradation could also be affected in temperate regions if global warming lead to drastic changes (Bouseba et al., 2009). For example, Levy et al. (2007) showed that the harsh summer conditions of 2003 altered the structure of the microbial communities involved in isoproturon biodegradation and decreased severely isoproturon mineralization. In colder regions, slight increase of temperature in spring and fall and more frequent freeze-thaw cycles due to climate change modify herbicide degradation and can drastically affect the availability for leaching (Benoit et al., 2007; Stenrød et al., 2005).

3.2 Abiotic degradation

Abiotic degradation of pesticides in soil has mainly been studied through laboratory experiments performed under controlled conditions. Identification of the reaction mechanisms and pathways is essentially performed using simplified matrix such as pure or commercial soil components. However the processes are ascertained in soils, through pesticide and its by-products monitoring, and evaluated through kinetic and comparative studies. Chemical reactions are generally performed using large amount of water in front of soils or soil components, but sometimes at realistic soil water content; dry soil matrixes are only used in photodegradation studies. To distinguish abiotic processes from biodegradation, soils are sterilized through various technics: generally autoclaving, but also adding biocide chemical (NaN_3, $HgCl_2$) or γ-irradiating with ^{60}Co. The influence of temperature on abiotic degradation will not be treated in this chapter. Globally it plays a role through adsorption-desorption equilibrium and Arrhenius law (Calvet et al., 2005).

3.2.1 Hydrolysis

Hydrolysis is defined as a chemical transformation by nucleophilic displacement of an organic compound RX with water to form ROH and a leaving group X (3):

$$RX + H_2O \rightarrow ROH + X^- + H^+ \tag{3}$$

In addition to reaction (3), hydrolytic reactions can be acid- or base-catalyzed (*ie* by H_3O^+ or OH- ions, respectively). Therefore, water availability and pH are key-factors for reaction occurrence and kinetics.

Hydrolysis may be favored by metal-ion catalysis, through two mechanisms: (i) direct polarization, where the metal coordinates the hydrolysable function (eventually through chelate formation) making it more electrophilic and thus more reactive and (ii) *in situ* generation of a reactive metal hydroxo species. Surface-bound metals may also catalyze hydrolysis according to those two mechanisms and a third one, where the electrostatic interactions enhance the OH^- concentration in the aqueous phase (Smolen & Stone, 1998). The most cited reactive metals are +II in solution (Cu(II), Pb(II), Mn(II), Fe(II),…) whereas +III or +IV as surface-bound or solid particulate species (goethite α-FeOOH, γ-Al_2O_3, TiO_2,…). Clay minerals also act as hydrolysis catalyzers, mainly because of their surface acidic pH. In the case of azinphosmethyl, cations involvement has been hypothesized to proceed from the formation of bidentate complex pesticide-clay interlayer cations, which increases P electrophilic character (Sánchez-Camazano & Sánchez-Martín, 1991). The role of soil organic matter on hydrolysis is complex, as the pesticides may be sorbed on the organic matter or dissolved in water: both states have to be considered but can hardly be distinguished experimentally. In the solution compartment, acid-catalyzed hydrolysis may be enhanced by acidic functional groups of the organic matter (Gamble & Khan, 1985). On the opposite, base-catalyzed processes may be inhibited because of the pollutant adsorbed status. This could be due to the negative charges associated with organic particles, which result in a decrease of the effective surface pH and/or stabilization of the transition species during reaction (Noblet et al., 1996). Organic matter effects may also be explained by a micellar catalysis model (Georgi et al., 2008). Furthermore, soil amendment with organic matter favors biodegradation and may hinder the effect of amendment on chemical hydrolysis reactions, as observed for triasulfuron by Said-Pullicino et al. (2004). However, those authors evidenced that this sulfonylurea degradation through (bio)hydrolysis was slightly reduced by compost amendment. Hydrolysis is a major degradation process for sulfonylureas in acidic soil (eventually more efficient than biodegradation), when their neutral form is prevalent: effect of soils parameters and potential pathways were reviewed by Sarmah & Sabadie (2002). Soil pH variation induces changes in sulfonylureas DT50 from less than 10 days to more than 100 days; soil moisture, clay or organic matter content act in a lesser extent on kinetics.

3.2.2 Oxidation and reduction

Oxidation and reduction correspond to reactions in which oxidation number (state) changes in a molecule (or ion, or atom): oxidation for its increase and reduction for its decrease. It can also be described by a loss or gain of electrons, respectively. Both types of reactions are systematically coupled, thus named redox reactions. Thus to oxidize (or reduce) a pesticide, there should be in the soil environment a chemical able to behave as oxidant/electron acceptor (or reductant/electron donor), *ie* presenting adequate redox potential.

Oxidation. Oxidative mechanisms in soils may be mediated by both oxidative enzymes (Dec & Bollag, 2000) and abiotic catalysts such as metal oxides. Among them, manganese oxides and hydroxides are major contributors because of their reactivity and frequency in soils (Li et al., 2003). Redox potentials of MnOOH and MnO_2 make those species able to oxidize organic contaminants with functionalities such as phenol (Lin et al., 2009), aniline (Laha & Luthy, 1990) or triazine (Shin & Cheney, 2004). In a lesser extent because of their lower potential, Fe(III) oxides or Fe(III) adsorbed on smectite clays may also act as oxidants (Li et al., 2003). The oxidation reaction begins with the formation of a precursor complex between

the pollutant and the surface-bound metallic species, followed by electron transfer within the complex and release of an organic cationic radical, that will evolve to an oxidized form or bind to a vicinal reactive species. Through the development of a mechanism-based kinetic model, Zhang et al. (2008) demonstrated that environmental factors may affect either the reaction kinetics of MnO_2-pollutant complex formation or the rate of electron transfer, directly or through action on the reactive surface sites. Among solutes, Mn(II) presents the strongest inhibitory effect, followed by other divalent cations as Ca^{2+} (Zhang et al., 2008). The pH plays a role by affecting ionizable pollutants and reactive surface sites, changing the speciation of MnO_2 surface. Organic matter may affect the reaction by reducing reactive surface sites through two processes: by contributing to the Mn-oxide reductive dissolution and by coating the mineral oxidant. Furthermore, it commonly reacts with the cationic radical and form covalent binding, resulting in bound residues (Li et al., 2000). Another abundant oxidizing agent in soil upper layers is oxygen, both in gaseous form and dissolved in liquid surface films. As a marginal pathway in soils, oxygen causes autooxidation or weathering through a radicalar mechanism involving $O_2^{-\bullet}$ production (Larson & Weber, 1994).

Reduction. In soils, pesticide reduction happens currently in suboxic and anoxic conditions encountered in poorly drained or groundwater-fed soils, riparian zones, wetlands or flooded areas and sediments. Nature of the reductants includes chemicals or "abiotic" reagents as reduced metal, sulfide ion or natural organic matter (Borch et al., 2010), but also extracellular biochemicals such as metal chelated in porphyrin or corrinoid or as transition-metal coenzymes (Kappler & Haderlein, 2003). Extensive studies using nitroaromatic contaminants as probe (such as trifluralin) showed that they are predominantly reduced by Fe(II) associated with iron minerals surfaces (Colon et al., 2006; Klupinski & Chin, 2003). Natural organic matter and particularly quinone moieties may also play a determinant role as an electron shuttle (Kappler & Haderlein, 2003). Furthermore, abiotic and biotic processes may be closely associated: Zhang & Weber (2009) demonstrated that reducible organic contaminants compete with iron oxides for the electron flow generated by the microbially mediated oxidation of organic carbon and subsequent reduction of quinone functional groups associated with dissolved organic matter.

3.2.3 Photodegradation

Photochemical reactions, *ie* reactions induced by UV or visible light, may degrade pesticides according to two types of processes, known as direct photolysis and indirect photodegradation. In direct photolysis, the pesticide itself absorbs light energy, becomes excited and, depending on the reaction activation energy, may undergo a transformation reaction. On the opposite, indirect photodegradation is defined as reaction of a ground-state pesticide with another photochemically produced species. This species can transfer energy, undergo an electron or hydrogen transfer, or lead to the formation of reactive entity (singlet oxygen, radical) which reacts with the pesticide. Reaction mechanisms and pathways were extensively reviewed in water and soil (Burrows et al., 2002; Katagi, 2004).

Light penetration in soil. The intensity and spectrum of sunlight reaching the soil depends on time of the day, season, latitude, altitude and state of the atmosphere (*eg* clouds or dust absorbing light), with shortest wavelength λ around 290 nm. In sunlight-exposed soils, photodegradation occurs within a shallow surface zone; its depth depends on soil characteristics and on the photodegradation mechanism. Hebert & Miller (1990) showed in

sandy loam soils that direct photolysis was restricted to 0.2-0.4 mm *ie* the photons penetration depth, while indirect process was deeper, 0.7 mm in mean but up to 2 mm or more due to the vertical migration by diffusion of active species and/or pesticide. Soil characteristics playing a role in photons penetration are essentially its light absorption and scattering by particles. Both vary with wavelength and moisture content (Ciani et al., 2005a). Through light absorption and scattering, soil texture plays a major role on light penetration: Gonçalves et al. (2006) found that higher porosity of a sandy soil in front of sandy loam ones may be responsible for the faster direct photolysis of quinalphos.

Direct photolysis. In direct photolysis, reaction kinetics (evaluated through degradation rate constant k) depends not only on the light intensity in the medium $I(\lambda)$ as upper mentioned, but also on the pesticide molar absorption coefficient $\varepsilon(\lambda)$ and on the quantum yield $\Phi(\lambda)$ of the chemical process (*ie* the efficiency by which photon energy is used for a chemical reaction) through equation (4):

$$k = \int_\lambda I(\lambda).\varepsilon(\lambda).\Phi(\lambda).d\lambda \qquad (4)$$

The functions $\varepsilon(\lambda)$ and $\Phi(\lambda)$ depend on the organic compound state, such as its ionization form and its sorption on soil components. Sorption may cause a bathochromic shift, reaching 45 nm for trifluralin on kaolinite or silica (Ciani et al., 2005b), and a hyperchromic shift is suspected (Ciani et al., 2005b; Menager et al., 2009). These modifications of $\varepsilon(\lambda)$ favour the photolytic process. The effect of sorption on quantum yield $\Phi(\lambda)$ has been evaluated by Ciani et al. (2005c) through the determination of $I(\lambda)$, $\varepsilon(\lambda)$, the diffusion parameters and the knowledge of degradation pathways, which may change with irradiation wavelength. They demonstrated that the quantum yield of 4-nitroanisole on kaolinite was on the same order of magnitude as in water, whereas that of trifluralin was 10 times smaller than in water. Furthermore, for aromatic compounds, triplet lifetimes are extended when adsorbed on silica or alumina, which means they may be more susceptible to photodegradation (Larson & Weber, 1994).

After solar light absorption, excited singlet states convert to triplet states (PX*) and undergo homolysis ($\rightarrow$ P• + X•), heterolysis ($\rightarrow$ P+ + X- or P- + X+) or photoionization ($\rightarrow$ PX+• + e_{aq}^-) (Burrows et al., 2002). The intermediate ions or radicals further evolve and lead to formation of by-products that may correspond to some also observed under other abiotic processes (*eg* photohydrolysis, photooxidation, deshalogenation) or to more specific by-products (*eg* photoisomerization, cyclization). According to reviews (Burrows et al., 2002; Katagi, 2004) the degradation schemes, although generally identical in water and soil, may present some singularities when the pesticide is adsorbed on soil. For instance, fipronil photodegradation scheme presents only one pathway in soil instead of two in water (Bobé et al., 1998a). Soil characteristics may play a different role according to the pesticide and its own properties: photodegradation efficiency was found to decrease when adsorption (Kf) increased for fipronil (Bobé et al., 1998a), or when pH increased for the sulfonylurea chlorimuron-ethyl (Choudhury & Dureja, 1997). Humic substances tend to decrease direct photolysis through light screening, static quenching (inhibition of the PX* formation through complexation of the ground-state molecule) and dynamic quenching (energy transfer from PX* to humic substance) (Walse et al., 2004). Specific study of direct photolysis in soil is complex because indirect processes may interfere, even if they can theoretically be distinguished through a two-steps kinetic model (Albanis et al., 2002; Hebert & Miller, 1990; Tajeddine et al., 2010).

Indirect photodegradation. In indirect photodegradation, soil components absorb sunlight and form a reactive species ($^3HS^*$ for humic substances HS) able to transfer energy, electron or hydrogen to the pesticide, or also to form a reactive intermediate that will degrade the pesticide (in the presence of water or oxygen: $^1O_2$, $^•OH$, $O_2^{-•}$ or its conjugate $HO_2^•$ (pKa 4.8), $^•OOR$, $^•OOH$ and/or H_2O_2). HS may play all those roles, but may also reduce indirect photodegradation by light screening and by scavenging the reactive species. The resulting effect can be a photodegradation increase (Albanis et al., 2002; Besse et al., 2005; Xiaozhen et al., 2005) or decrease (Albanis et al. 2002; Tajeddine et al., 2010). Non-transition metal oxides such as aluminium oxide or magnesium oxide can photocatalyze the $^1O_2$ generation (Gohre & Miller, 1985). Transition metals such as iron and manganese, under oxide or hydroxide forms or included in clays, can act as quenchers or as catalytic sites for reactions, as electron mediators. In the presence of water, iron plays a great role in generating $^•OH$, mostly through photo-Fenton reaction (Fe(II)/H_2O_2) or by reaction of a Fe(III)-HS complex. Clay minerals are also known to act on photodegradation. Existing literature tends to attribute their role to: 1) their sorption properties to retain pesticides at soil surface, 2) the bathochromic (and maybe hyperchromic) effects of sorption, 3) $^1O_2$, $O_2^{-•}$ and $^•OH$ active species formed by irradiation of clay in the presence of water and/or oxygen, 4) screen effect and steric constraint that photostabilize the sorbed pesticide, 5) charge or energy transfer of the photoexcited clay to the pesticide or of the photoexcited pesticide to the clay, and 6) clays content and coating in (by) reactive metallic species and HS, forming clay-(metal)-HS complexes. Points 1, 2 and 3 favour the photodegradation, 4 decreases it, whereas the two other may result in an increase or a decrease of the photoprocesses. Photodegradation enhancement by 6 is linked to $^•OH$ generation by free and structural irons under Fe(II) and Fe(III) forms (Wu et al., 2008). In soil, clay-metal-HS complexes may also decrease photodegradation, because of Fe(III) efficiency as energy or charge acceptor (Rozen & Margulies, 1991; Mountacer et al., 2011). Furthermore, as HS, silicate surface may trap peroxy radicals and thus lessen the process on soil surfaces.

Effect of soil water content. Water plays a major role, directly as a reactant to form active species such as $^•OH$ or indirectly as a solvent, favouring presence of precursor chemicals (for instance metallic ions) and diffusion. Therefore, if the soil is dry, there is far less possibility of indirect photodegradation. On the opposite, as light penetrates more deeply through the interstitial spaces of dry soil (Ciani et al., 2005a; Frank et al., 2002), direct photolysis could be favoured by dryness. However, the global resulting pesticide photodegradation has largely been demonstrated to be slower in dry soils, with half-lives multiplied by a 2-7 factor or more (Frank et al., 2002; Graebing et al., 2003). Relative importance of the degradation pathways can also be influenced by the presence of water, for instance if a photohydrolysis mechanism is involved (Tajeddine et al., 2010). Drying/rewetting cycles favour indirectly the photodegradation process, because of the movement of the pesticide through condensation and evaporation (Frank et al., 2002).

Using atrazine as a probe, Xiaozhen et al. (2005) showed that photodegradation on soil was enhanced by: presence of water (facilitating movements), acidic or alkaline soil pH (H^+ and OH^- catalyzing reactions), smaller particle size (higher catalytic surface area), higher humic acid content and presence of a surface-active agent that increase pesticide solubilization. Agricultural practices, such as addition of fertilizer or compost, may modify the photodegradation processes. However, even if nitrate ions are major photoinducers in natural waters (Nélieu et al., 2009 and references therein), their addition

in soil does not increase photodegradation (Graebing et al., 2002). Compared to surrounding soil, earthworm casts were found to favour the atrazine photodegradation and make it preeminent in front of biodegradation (Besse et al., 2005), maybe because of changes in organic matter and minerals in casts. When compared to other biotic and abiotic degradation processes, the photodegradation may be dominant on dry, sunlight-exposed surfaces while other dissipation pathways prevail in deeper layers (Hebert & Miller 1990; Dimou et al., 2004). *In situ* experiments showed that by-products issuing from fipronil appeared in the following order over time: photodegradates, products of oxidation and eventually reduction, and products resulting from (bio)-hydrolysis (Bobé et al., 1998b).

4. Relevant scale and influent integrated factors

Macromolecular scale. Humic substances are now seen as an assemblage of small molecular weight components. The structure of organic matter is governed by its macromolecular nature and the competition between polar and apolar interactions depending on the physico-chemical environment (Sutton & Sposito, 2005). Hydrophobic structures such as flexible micelle-like structure involve intra-chain interactions, and rigid condensed phase includes inter-chain interactions (Chassenieux et al., 2000). Micelle-like structure is rather associated to aliphatic carbon, and condensed phase involves preferentially aromatic carbons (Huang et al., 2003). The polarity of organic mater can be estimated by O+N/C atomic ratio and by its aromaticity H/C ratio (Xing et al., 1994). Structural descriptors, using ^{13}C NMR techniques complete this description by determining the percentages of aromatic-, aliphatic- carboxyl- and carbonyl-C (Ahangar et al., 2008; Xing & Pignatello, 1997). The interaction of less polar pollutants with the micelle-like structure is a partitioning process characterized by linear isotherm and reversible behaviour (Sierra et al., 2005). Polar contributions between aromatic rings and substituted monoaromatic π systems increase the energy, enhance the non linearity of isotherms and hysteresis (Keiluweit & Kleber, 2009; Schlautman & Morgan, 1993). But no significant correlation between aromaticity or aliphaticity and sorption affinity was established (Chefetz & Xing, 2009; Pan et al., 2008a). The local molecular organization has to be considered (Ahangar et al., 2008; Huang et al., 2003; Jung et al., 2010).

Organo-clay complex. The organo-clay complex refers to the granulometric fraction < 2 μm. In soils, the clay surface was found to be completely saturated in carbon (Séquaris et al., 2010). In this fraction, the organic matter is present in dissolved and sorbed phases. Sorption of organic matter on clay minerals can be seen as a fractionating process because high molecular weight polymers are preferentially adsorbed (Pan et al., 2008b). High molecular weight and high surface area confer to the organo-clay complex a major role towards the retention of pesticides in soils. For example, the wettability of the clay fraction, characterized by the contact angle θ of water drop deposed on a thin air dried film, is directly related to the retention of diuron by the soil (Chaplain et al., 2008). The cosθ is related to the liquid and solid interactions by the Young–Dupré equation and the polar and apolar components of these interactions can be measured using appropriate solvents (Van Oss, 1994). We suggest that diuron can be used as a reference pesticide to characterize the global hydrophobicity of soil due to its high chemical stability in a large range of pH (Chaplain et al., 2008). Finally, as drying is known to enhance soil hydrophobicity (Diehl et al., 2009), an increase in the sorption of pesticide by re-wetting

soils is expected but this is poorly described (Lennartz & Louchart, 2007). Biological processes are also affected by wettability (Braun et al., 2010).

Aggregate scale or micro-habitat. Soil characteristics measured on bulk soil samples poorly reflect the local environmental conditions experienced by microorganisms (Christensen et al., 1990). Microorganisms' sizes range from the micrometer (bacteria) to millimetres or centimetres (fungi). The spatial heterogeneity of soil conditions at this micro-habitat scale directly influences their activity but is rarely taken into account (Parkin, 1993). In particular, the rate of biodegradation depends on the presence of specific microorganisms, the bioavailability of the compound (adsorbed or not, physically accessible or not), and on favourable environmental conditions. Each of these factors may be heterogeneous at the microscale. For example, studies of the mineralization of 2,4-D in a silty soil at microbial habitat scale showed that mineralization was spatially heterogeneous and that its variability increased when the size of micro-habitats decreased (Vieublé-Gonod et al., 2006).

Mesoscopic scale. Mesoscopic scale (around 100 cm^3) appears as the pertinent transition scale between laboratory studies and field measurements. In any cases, the water status, including the water distribution into the heterogeneous soil structure, can be controlled by imposing a given water potential. The integrative measurable parameters at this scale are the bulk density and the water content of soil samples. Our recent results confirm that this scale is suited to study the effects of soil structure on the fate of pesticide (Mamy et al., 2011). This scale is also appropriate to measure, in an integrative manner, the fate and ecotoxicological impact of pesticides in conditions close to the field ones. Finally, this scale is also relevant to study the effect of agricultural practices on bulk density: contrasted effects of no-till were shown with various soils. As mechanical properties of soil are closely related to soil structure and water content, we also found that the variation of these properties with the initial bulk density of soil is a good tool to predict the long-term effect of no-till on bulk density for various soils (Chaplain et al., 2011).

Plot scale. At the plot scale, our results showed that 2,4-D mineralization variability decreased when compared to micro-habitat scale (Vieublé Gonod et al., 2006). At this scale, the location of the added organic matter in soil is an important controlling factor. Indeed, the incorporation of crop residues or organic amendments by ploughing induces a heterogeneous spatial distribution of the added organic matter in the tilled layer. The effects of this spatial variation on the fate of isoproturon have been assessed by Vieublé-Gonod et al. (2009). They showed that interfurrows, containing important quantities of fresh organic matter, constituted a special local environment with the highest level of microbial biomass and the highest isoproturon mineralizing capacities and respiration levels. The presence of compost in the interfurrows stimulated isoproturon biodegradation relative to controls. This effect was more pronounced for the municipal solid waste compost than for the co-compost of green waste and sewage sludge. Heterogeneity may persist several months after compost or stubble hiding depending on the nature of added organic matter. Another important driver of heterogeneity at the plot scale is linked to water retention properties as shown for the degradation of glyphosate (Stenrød et al., 2006) and isoxaflutole (Alletto et al., 2008).

5. Conclusion

The fate of pesticides in the environment is mainly regulated by their behaviour in soils, and in particular by their adsorption and biotic and abiotic degradation. The extent of these

processes depends on the physico-chemical properties of pesticides (electronic structure, solubility…) and on the soil properties (constituents, structure at different scales…). They also strongly depend on the environmental conditions like temperature and water content. To improve the understanding of the fate of pesticides in soils, there is a need to better take into account the soils heterogeneity and variability. Studies have to consider relevant integrative parameters describing the soil structure and interfacial properties at various water contents. Depending on the scale, integrative parameters are, in increasing order: hydrophobic structures of organic matter, wettability of clay fraction, soil hydrophobicity, bulk density related to water retention and physical properties like mechanical resistance, hydraulic conductivity and water retention, and spatial repartition of exogenous organic matter. The water content and its distribution in heterogeneous structures should be considered simultaneously. In the perspective of the reduction of pesticide use, the main options are the choice of pesticide and of its commercial formulation, and the improvement of agricultural practices. To evaluate their effects, we propose to use the mesoscopic scale as a link between molecular and field scales, because it allows measurements of coupled processes with any kind of materials, including structured soils. Finally, the effects of wet-dry cycles on the fate of pesticides are poorly known and deserve to be studied in view of climate change.

6. References

Ahangar, A.G.; Smernik, R.J.; Kookana, R.S. & Chittleborough, D.J. (2008). Clear effects of soil organic matter chemistry, as determined by NMR spectroscopy, on the sorption of diuron. *Chemosphere*, Vol. 70, No.7, pp. 1153-1160

Albanis, T.A.; Bochicchio, D.; Bufo, S.A.; Cospito, I.; D'Auria, M.; Lekka, M. & Scrano, L. (2002). Surface adsorption and photo-reactivity of sulfonylurea herbicides. *International Journal of Environmental Analytical Chemistry*, Vol.82, No.8-9, pp.561-569

Alletto, L.; Coquet, Y.; Benoit, P. & Bergheaud, V. (2006). Effects of temperature and water content on degradation of isoproturon in three soil profiles. *Chemosphere*, Vol.64, No.7, pp.1053–1061

Alletto, L.; Benoit, P.; Bergheaud, V. & Coquet, Y. (2008). Tillage, temperature and water content effects on the degradation of the diketonitrile metabolite of isoxaflutole in a Gleyic Luvisol. *Environmental Pollution*, Vol.156, No.3, pp.678-688

Alletto, L.; Coquet, Y. & Roger-Estrade, J. (2010a). Two-dimensional spatial variation of soil physical properties in two tillage systems. *Soil Use & Management*, Vol.26, No.4, pp. 432-444

Alletto L.; Coquet, Y.; Benoit P.; Heddadj, D. & Barriuso, E. (2010b). Tillage management effects on pesticide fate in soils. A review. *Agronomy for Sustainable Development*, Vol.30, No.2, pp.367-400

Baldrian, P. (2009). Microbial enzyme-Catalyzed processes in soils and their analysis. *Plant Soil & Environment*, Vol.55, No.9, pp.370-378

Barriuso, E.; Laird, D.A.; Koskinen, W.C. & Dowdy, R.H. (1994). Atrazine desorption from smectites. *Soil Science Society of America Journal*, Vol.58, No.6, pp.1632-1638

Barriuso, E.; Benoit, P. & Dubus, I.G. (2008). Formation of pesticide nonextractable (bound) residues in soils: magnitude, controlling factors and reversibility. *Environmental Science & Technology*, Vol.42, No.6, pp.1845-1854

Bastos, A.C. & Magan, N. (2009). Trametes versicolor: potential for atrazine bioremediation in calcareous clay soil, under low water availability conditions. *International Biodeterioration & Biodegradation*, Vol.63, No.4, pp.389-394

Benoit, P.; Barriuso, E.; Vidon, P. & Réal, B. (2000). Isoproturon movement and dissipation in undisturbed soil cores from a grassed buffer strip. *Agronomie*, Vol.20, No.3, pp.297-307

Benoit, P.; Perceval, J.; Stenrød, M.; Moni, C.; Eklo, O.M.; Barriuso, E.; Sveistrup, T. & Kværner J. (2007). Availability and biodegradation of metribuzin in sandy loam soils as affected by temperature and soil properties. *Weed Research*, Vol.47, No.6, pp.517-526

Benoit, P.; Madrigal, I.; Preston, C.M.; Chenu, C. & Barriuso, E. (2008). Sorption and desorption of non-ionic herbicides onto particulate organic matter from surface soils under different land uses. *European Journal of Soil Science*, Vol.59, No.2, pp.178-189

Besse, P.; Sancelme, M.; Delort, A.M.; Aguer, J.P.; Lavédrine, B.; Richard, C.; Alekseeva, T.; Taviot-Guého, C.; Forano, C.; A. Kersanté, A.; Josselin, N. & Binet, F. (2005). Photo- and biodegradation of atrazine in the presence of soil constituents. In: *Environmental chemistry: green chemistry and pollutants in ecosystems*, E. Lichtfouse, J. Schwarzbauer, D. Robert (Eds.), pp. 473-482, Springer, ISBN 3-540-22860-8, Berlin, Heidelberg, New York

Beulke, S.; Brown, C.D.; Fryer, C.J. & van Beinum, W. (2004). Influence of kinetic sorption and diffusion on pesticide movement through aggregated soils. *Chemosphere*, Vol.57, No.6, pp. 481-490

Bobé, A.; Meallier, P.; Cooper, J.F. & Coste, C.M. (1998a). Kinetics and mechanisms of abiotic degradation of fipronil (hydrolysis and photolysis). *Journal of Agricultural & Food Chemistry*, Vol.46, No.7, pp.2834-2839

Bobé, A.; Cooper, J.F.; Coste, C.M. & Muller, A.M. (1998b). Behaviour of fipronil in soil under Sahelian plain field conditions. *Pesticide Science*, Vol.52, No.3, pp.275-281

Bollag, J.-M. & Liu, S.-Y. Biological transformation of pesticides. In: *Pesticides in the Soil Environment* (Soil Science Society of America, Madison, 1990), Chap.6, pp.169-211

Borch, T.; Kretzschmar, R.; Kappler, A.; van Cappellen, P.; Ginder-Vogel, M.; Voegelin, A. & Campbell, K. (2010). Biogeochemical redox processes and their impact on contaminant dynamics. *Environmental Science & Technology*, Vol.44, No.1, pp.15-23

Bouseba, B.; Zertal, A.; Beguet, J.; Rouard, N.; Devers, M.; Martin, C. & Martin-Laurent, F. (2009). Evidence for 2,4-D mineralisation in Mediterranean soils: impact of moisture content and temperature. *Pest Management Science*, Vol.65, No.9, pp.1021-1029

Braun, B.; Böckelmann, U.; Grohmann, E. & Szewzyk, U. (2010). Bacterial soil communities affected by water-repellency. *Geoderma*, Vol.158, No.3/4, pp.343-351

Burrows, H.D.; Canle L., M.; Santaballa, J.A. & Steenken, S. (2002). Reaction pathways and mechanisms of photodegradation of pesticides. *Journal of Photochemistry & Photobiology B: Biology*, Vol.67, No.2, pp.71–108

Cabidoche, Y.M.; Achard, R.; Cattan, P.; Clermont-Dauphin, C.; Massat, F. & Sansoulet, J. (2009). Long-term pollution by chlordecone of tropical volcanic soils in the French West Indies: A simple leaching model accounts for current residue. *Environmental Pollution*, Vol.157, No.5, pp.1697-1705

Calvet, R. (1989). Adsorption of organic chemicals in soils. *Environmental Health Perspectives*, Vol.83, pp.145-177

Calvet, R.; Barriuso, E.; Bedos, C.; Benoit, P.; Charnay, M.P. & Coquet, Y. (2005). *Les pesticides dans les sols. Conséquences agronomiques et environnementales* (Editions France Agricole), Dunod, ISBN 2-85557-119-7, Paris

Celis, R.; Barriuso, E. & Houot, S. (1998). Effect of sewage sludge addition on atrazine sorption and desorption by soil. *Chemosphere*, Vol.37, No.6, pp.1091-1107

Chaplain, V.; Brault, A. ; Tessier, D. & Défossez, P. (2008). Soil hydrophobicity: a contribution of diuron sorption experiments. *European Journal of Soil Science*, Vol.59, No.6, pp.1202-1208

Chaplain, V.; Défossez, P.; Richard, G.; Tessier, D. & Roger-Estrade, J. (2011). Contrasted effects of no-till on bulk density of soil and mechanical resistance. *Soil & Tillage Research*, Vol.111, No.2, pp.105-114

Chassenieux, C.; Fundin, J.; Ducouret, G. & Iliopoulos, I. (2000). Amphiphilic copolymers of styrene with a syrfactant-like comonomer: gel formation in aqueous solution. *Journal of Molecular Structure*, Vol.554, No.1, pp. 99-108

Chefetz, B. & Xing, B.S. (2009). Relative Role of Aliphatic and Aromatic Moieties as Sorption Domains for Organic Compounds: A Review. *Environmental Science & Technology* Vol. 43, No.6, pp.1680-1688

Choudhury, P.P. & Dureja, P.D. (1997). Studies on photodegradation of chlorimuron-ethyl in soil. *Pesticide Science*, Vol.51, No.2, pp.201-205

Christensen, S.; Simkins, S. & Tiedje, J.M. (1990). Spatial variation in denitrification: dependency of activity centers on the soil environment. *Soil Science Society of America Journal*, Vol.54, No.6, pp.1608-1613

Ciani, A.; Goss, K.U. & Schwarzenbach, R.P. (2005a). Light penetration in soil and particulate minerals. *European Journal of Soil Science*, Vol.56, No.5, pp.561-574

Ciani, A.; Goss, K.U. & Schwarzenbach, R.P. (2005b). Determination of molar absorption coefficients of organic compounds adsorbed in porous media. *Chemosphere*, Vol.61, No.10, pp.1410-1418

Ciani, A.; Goss, K.U. & Schwarzenbach, R.P. (2005c). Photodegradation of organic compounds adsorbed in porous mineral layers: determination of quantum yields. *Environmental Science & Technology*, Vol.39, No.17, pp.6712-6720

Colón, D.; Weber, E.J.; Anderson, J.L.; Winget, P. & Suárez, L.A. (2006). Reduction of nitrosobenzenes and N-hydroxylanilines by Fe(II) species: elucidation of the reaction mechanism. *Environmental Science & Technology*, Vol.40, No.14, pp.4449-4454

Coquet, Y. & Barriuso, E. (2002). Spatial variability of pesticide adsorption within the topsoil of a small agricultural catchment. *Agronomie*, Vol.22, No.4, pp.389-398

Cox, L. & Walker, A. (1999). Studies of time-dependent sorption of linuron and isoproturon in soils. *Chemosphere*, Vol.38, No.12, pp.2707-2718

Dec, J. & Bollag, J.M. (2000) Phenoloxidase-mediated interactions of phenols and anilines with humic materials. *Journal of Environmental Quality*, Vol.29, No.3, pp.665-676

Diehl, D.; Ellerbrock, R.H. & Schaumann, G.E. (2009). Influence of drying conditions on wettability and DRIFT spectroscopic C-H band of soil samples. *European Journal of Soil Science*, Vol.60, No.4, pp.557-566

Dimou, A.D.; Sakkas, V.A. & Albanis, T.A. (2004). Photodegradation of trifluralin in natural waters and soils: Degradation kinetics and influence of organic matter. *International Journal of Environmental Analytical Chemistry*, Vol.84, No.1-3, pp.173-182

Duquenne, P.; Parekh, N.R.; Catroux, G. & Fournier, J.C. (1996). Effect of inoculant density, formulation, dispersion and soil nutrient amendment on the removal of carbofuran residues from contaminated soil. *Soil Biology & Biochemistry*, Vol. 28, No., pp.1805-1811

Frank, M.P.; Graebing, P. & Chib, J.S. (2002). Effect of soil moisture and sample depth on pesticide photolysis. *Journal of Agricultural & Food Chemistry*, Vol.50, No.9, pp.2607-2614

Gaillardon, P. & Dur J.C. (1995). Influence of soil moisture on short-term adsorption of diuron and isoproturon by soil. *Pesticide Science*, Vol.45, No.4, pp.297-303

Gamble, D.S. & Khan, S.U. (1985). Atrazine hydrolysis in soils: catalysis by the acidic functional groups of fulvic acid. *Canadian Journal of Soil Science*, Vol.65, No.3, pp.435-443

Georgi, A.; Trommler, U.; Reichl, A. & Kopinke, F.D. (2008). Influence of sorption to dissolved humic substances on transformation reactions of hydrophobic organic compounds in water. Part II: Hydrolysis reactions. *Chemosphere*, Vol.71, No.8, pp.1452-1460

Gohre, K. & Miller, G.C. (1985). Photochemical generation of singlet oxygen on non-transient-metal oxide surfaces. *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases*, Vol.81, No.3, pp.793-800

Gonçalves, C.; Dimou, A.; Sakkas, V.; Alpendura, M.F. & Albanis, T.A. (2006). Photolytic degradation of quinalphos in natural waters and soil matrices under simulated solar irradiation. *Chemosphere*, Vol.64, No. 8, 1375-1382

Graebing, P.; Frank, M. & Chib, J.S. (2002). Effects of fertilizer and soil components on pesticide photolysis. *Journal of Agricultural & Food Chemistry*, Vol.50, No.25, pp.7332-7339

Graebing, P.; Frank, M.P. & Chib, J.S. (2003). Soil photolysis of herbicides in a moisture- and temperature-controlled environment. *Journal of Agricultural & Food Chemistry*, Vol.51, No.15, pp.4331-4337

Hebert, V.R. & Miller, G.C. (1990). Depth dependence of direct and indirect photolysis on soil surfaces. *Journal of Agricultural & Food Chemistry*, Vol.38, No.3, pp.913-918

Huang, W.; Peng, P.; Yu, Z. & Fu, J. (2003). Effects of organic matter heterogeneity on sorption and desorption of organic contaminants by soils and sediments. *Applied Geochemistry,* Vol.18, No.7, pp.955-972

Jung, A.V., Frochot, C., Villieras, F., Lartiges, B.S., Parant, S., Viriot, M.-L. & Bersillon, J.-L. (2010). Interaction of pyrene fluoroprobe with natural and synthetic humic

substances : examining the local molecular organization from photophysical and interfacial processes. *Chemosphere*, Vol.80, No.3, pp.228-234

Kappler, A. & Haderlein, S.B. (2003). Natural organic matter as reductant for chlorinated aliphatic pollutants. *Environmental Science & Technology*, Vol.37, No.12, pp.2714-2719

Katagi, T. (2004). Photodegradation of pesticides on plant and soil surfaces. *Reviews of Environmental Contamination & Toxicology,*Vol.182, pp.1-195, ISBN 978-0-387-20845-9

Keiluweit, M. & Kleber, M. (2009). Molecular-Level Interactions in Soils and Sediments: The Role of Aromatic Ï€-Systems. *Environmental Science & Technology*, Vol.43, No.10, pp.3421-3429

Kier, L.B. & Hall, L.H. (2000). Intermolecular accessibility: the meaning of molecular connectivity. *Journal of Chemical Information & Computer Sciences*, Vol.40, pp.792-795

Klupinski, T.P. & Chin, Y.P. (2003). Abiotic degradation of trifluralin by Fe(II): kinetics and transformation pathways. *Environmental Science & Technology*, Vol.37, No.7, pp.1311-1318

Koskinen, W.C.; Cox, L. & Yen, P.Y. (2001). Changes in sorption/bioavailability of imidacloprid metabolites in soil with incubation time. *Biology & Fertility of Soils*, Vol.33, No.6, pp.546-550

Laha, S. & Luthy, R.G. (1990). Oxidation of aniline and other primary aromatic amines by manganese dioxide. *Environmental Science & Technology*, Vol.24, No.3, pp.363-373

Larsbo, M.; Stenström, J.; Etana, A.; Börjesson, E. & Jarvis, N.J. (2009). Herbicides sorption, degradation, and leaching in three Swedish soils under long-term conventional and reduced tillage. *Soil & Tillage Research*, Vol.105, No.2, pp.200-208

Larson, R.A. & Weber, E.J. (1994) *Reaction mechanisms in environmental organic chemistry*, Lewis Publishers, ISBN 0-87371-258-7, Boca Raton, Florida

Lennartz, B. (1999). Variation of herbicide transport parameters within a single field and its relation to water flux and soil properties. *Goederma*, Vol.91, No.3-4, pp.327-345

Lennartz, B. & Louchart, X. (2007). Effect of drying on the desorption of diuron and terbuthylazine from natural soils. *Environmental Pollution,* Vol. 146 No.1, pp.180-187

Levy, W.; Radl, V.; Ruth, B.; Schmid, M.; Munch, J.C. & Schroll, R. (2007). Harsh summer conditions caused structural and specific functional changes of microbial communities in an arable soil. *European Journal of Soil Science*, Vol.58, No.3, pp.736-745

Li, H.; Lee, L.S.; Jafvert, C.T. & Graveel, J.G. (2000). Effect of substitution on irreversible binding and transformation of aromatic amines with soils in aqueous systems. *Environmental Science & Technology*, Vol.34, No.17, pp.3674-3680

Li, H.; Lee, L.S.; Schulze, D.G. & Guest, C.A. (2003). Role of soil manganese in the oxidation of aromatic amines. *Environmental Science & Technology*, Vol.37, No.12, pp.2686-2693

Lin, K.; Liu, W. & Gan, J. (2009). Reaction of tetrabromobisphenol A (TBBPA) with manganese dioxide: kinetics, products, and pathways. *Environmental Science & Technology*, Vol.43, No.12, pp.4480–4486

Linn, D.M. & Doran, J.W. (1984). Aerobic and anaerobic microbial populations in no-till and plowed soils. *Soil Science Society of America Journal*, Vol.48, No.4, pp.794-799.
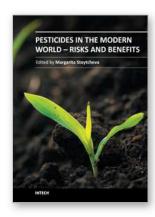
Liu, W.; Gan, J.; Papiernik, S.K. & Yates, S.R. (2000). Structural influences in relative sorptivity of choloroacetalinide herbicides on soil. *Journal of Agricultural & Food Chemistry*, Vol.48, No.9, pp.4320-4325

McConnell, J.S. & Hossner, L.R. (1985). pH-dependent adsorption isotherms of glyphosate. *Journal of Agricultural & Food Chemistry*, Vol.33, No.6, pp.1075-1078

Mamy, L. & Barriuso, E. (2005). Glyphosate adsorption in soils compared to herbicides replaced as a result of the introduction of glyphosate resistant crops. *Chemosphere*, Vol.61, No.6, pp.844-855

Mamy, L. & Barriuso, E. (2007). Desorption and time-dependent sorption of herbicides in soils. *European Journal of Soil Science*, Vol.58, No.1, pp.174-187

Mamy, L.; Vrignaud, P.; Cheviron, N.; Perreau, F.; Belkacem, M.; Brault, A.; Breuil, S.; Delarue, G.; Pétraud, J.P.; Touton, I.; Mougin, C. & Chaplain, V. (2011). No evidence for the effect of soil compaction on the degradation and impact of isoproturon. *Environmental Chemistry Letters*, Vol.9, No.1, pp.145-150

Mapa, R.B.; Green, R.E. & Santo, L. (1986). Temporal variability in soil hydraulic properties with wetting and drying subsequent to tillage. *Soil Science Society of America Journal*, Vol. 50, 1133–1138

Mermoud, A.; Martins, J.M.F.; Zhang, D. & Favre, A.C. (2008). Small-scale spatial variability of atrazine and dinoseb adsorption parameters in an alluvial soil. *Journal of Environmental Quality*, Vol.37, No.5, pp.1927-1936

Menager, M.; Siampiringue, M. & Sarakha, M. (2009). Photochemical behaviour of phenylbenzoquinone at the surface of the clays: kaolinite, bentonite and montmorillonite. *Journal of Photochemistry & Photobiology A: Chemistry*, Vol.208, No.2-3, pp.159–163

Monard, C.; Nunan, N.; Bardoux, G. & Vieublé-Gonod, L. (2010). A miniaturised method to quantify microbial mineralisation of 13C-labelled organic compounds in small soil samples. *Soil Biology & Biochemistry*, Vol. 42, No.9, pp.1640-1642

Morillo, E.; Undabeytia, T.; Maqueda, C. & Ramos, A. (2000). Glyphosate adsorption on soils of different characteristics. Influence of copper addition. *Chemosphere*, Vol.40, No.1, pp.103-107

Mougin C. (2002). Bioremediation and phytoremediation of industrial PAH-polluted soils. *Polycyclic Aromatic Compounds*, Vol.22, No., pp.1011-1043

Mountacer, H.; Tajeddine, L. & Sarakha, M. (2011). Adsorption and photochemical behavior of the herbicide monuron on clay surfaces, In: *Herbicides and environment*, Kortekamp A., 273-294, Intechweb.org

Nam, K.; Chung, N.H. & Alexander, M. (1998). Relationship between organic matter content of soil and the sequestration of phenanthrene. *Environmental Science & Technology*, Vol.32, No.23, pp.3785-3788

Naumann, K. (2000). Influence of chlorine substituents on biological activity of chemicals: a review. *Pest Management Science*, Vol.56, No.1, pp.3-21

Nélieu, S.; Perreau, F.; Bonnemoy, F.; Ollitrault, M.; Azam, D.; Lagadic, L.; Bohatier, J. & Einhorn, J. (2009). Sunlight nitrate-induced photodegradation of chlorotoluron: evidence of the process in aquatic mesocosms. *Environmental Science & Technology*, Vol.43, No.9, pp.3148-3154

Noblet, J.A.; Smith, L.A. & Suffet, I.H.M. (1996). Influence of natural dissolved organic matter, temperature and mixing on the abiotic hydrolysis of triazine and organophosphate pesticides. J*ournal of Agricultural & Food Chemistry*, Vol.44, No.11 pp.3685–3693.

OECD (2008a). Guidance document for the performance of out-door monolith lysimeter studies. OECD Series on Testing and Assessment, Number 22. Organization for Economic Cooperation and Development, Paris

OECD (2008b). OECD 106. Guideline for the testing of chemicals. Adsorption-desorption using a batch equilibrium method. Organization for Economic Cooperation and Development, Paris

OECD (2002). Guideline for the testing of chemicals. Aerobic and anaerobic transformation in soil. Organization for Economic Cooperation and Development, Paris

Pan, B.; Ning, P. & Xing, B., (2008a). Humic substances. Review series. Part IV-sorption of hydrophobic organic contaminants. *Environmental Science & Pollution Research*, Vol.15, No.7, pp.554-564

Pan, B.; Tao, S.; Dawson, R.W. & Xing, B.S. (2008b) Formation of organo-mineral complexes as affected by particle size, pH, and dry-wet cycles. *Australian Journal of Soil Research*, Vol.48, No.8, pp.713-719

Parkin, T.B. (1993). Spatial variability of microbial processes in soil—a review. *Journal of Environmental Quality*, Vol.22, No.3, pp.409–416

Pot, V.; Simunek J.; Benoit P.; Coquet Y.; Yra A. & Martinez-Cordon M.J. (2005). Impact of rainfall intensity on the transport of two herbicides in undisturbed grassed filter strip soil cores. *Journal of Contaminant Hydrology*, Vol.81, No.1/4, pp.63-88

Pot, V.; Benoit, P.; Menn, M.L.; Eklo, O.M.; Sveistrup, T. & Kvaerner, J. (2011). Metribuzin transport in undisturbed soil cores under controlled water potential conditions: experiments and modelling to evaluate the risk of leaching in a sandy loam soil profile. *Pest Management Science*, Vol.67, No.4, pp.397-407

Qureshi, A.; Mohan, M.; Kanade, G.S.; Kapley, A.; Purohit, H.J. & Hemant, J. (2009). In situ bioremediation of organochlorine-pesticide-contaminated microcosm soil and evaluation by gene probe. *Pest Management Science*, Vol. 65, No.7, pp.798-804

Roy, C.; Gaillardon, P. & Montfort, F. (2000). The effect of soil moisture content on the sorption of five sterol biosynthesis inhibiting fungicides as a function of their physicochemical properties. *Pest Management Science*, Vol.56, No.9, pp.795-803

Rozen, H. & Margulies, L. (1991). Photostabilization of tetrahydro-2-(nitromethylene)-2H-1,3-thiazine adsorbed on clays. *Journal of Agricultural & Food Chemistry*, Vol.39, No.7, pp.1320-1325

Sabljic, A.; Güsten, H.; Verhaar, H. & Hermens, J. (1995). QSAR modelling of soil sorption. Improvements and systematics of log Koc vs. log Kow correlations. *Chemosphere*, Vol.31, No.11-12, pp.4489-4514

Said-Pullicino, D.; Gigliotti, G. & Vella, A.J. (2004). Environmental fate of triasulfuron in soils amended with municipal waste compost. *Journal of Environmental Quality*, Vol.33, No.5, pp.1743-1751

Saison C.; Cattan P.; Louchart X. & Voltz. M. (2008). Effect of Spatial Heterogeneities of Water Fluxes and Application Pattern on Cadusafos Fate on Banana-Cultivated Andosols. *Journal of Agricultural & Food Chemistry*, Vol.56, No.24, pp.11947–11955

Sánchez-Camazano, M. & Sánchez-Martín, M.J. (1991). Hydrolysis of azinphosmethyl induced by the surface of smectites. *Clays & Clay Minerals*, Vol.39, No.6, pp.609-613

Sarmah, A.K. & Sabadie, J. (2002). Hydrolysis of sulfonylurea herbicides in soils and aqueous solutions: a review. *Journal of Agricultural & Food Chemistry*, Vol.50, No.22, pp.6253-6265

Schlautman, M.A. & Morgan, J.J. (1993). Binding of a fluorescent hydrophobic organic probe by dissolved humic substances and organically-coated aluminium oxide particles. *Environmental Science & Technology*, Vol.27, No.12, pp.2523-2532

Schroll, R.; Becher, H.H.; Dorfler, U.; Gayler, S.; Grundmann, S.; Hartmann, H.P. & Ruoss, J. (2006). Quantifying the effect of soil moisture on the aerobic microbial mineralization of selected pesticides in different soils. *Environmental Science & Technology*, Vol.40, No.10, pp.3305-3312

Séquaris, J.-M.; Guisado, G.; Magarinos, M.; Moreno, C.; Burauel, P.; Narres, H.-D. & Vereecken, H. (2010). Organic-carbon fractions in an agricultural topsoil assessed by the determination of the soil mineral surface area. *Journal of Plant Nutrition & Soil Science*, Vol.173, No.5, pp.699-705

Shaw, L.J.; Beaton, Y.; Sousa, S.; Glover, L.A.; Killham, K. & Meharg, A.A. (2002). Mineralisation of 2,4-dichlorophenol and glucose placed into the same or different hydrological domains as a bacterial inoculant. *Soil Biology & Biochemistry*, Vol.34, No.4, pp.531-539

Shin, J.Y. & Cheney, M.A. (2004). Abiotic transformation of atrazine in aqueous suspension of four synthetic manganese oxides. *Colloids & Surfaces A: Physicochemical and Engineering Aspects*, Vol.242, No.1-3, pp. 85–92

Sierra, M.M.D.; Rauen, T.G.; Tormen, L.; Debacher, N.A. & Soriano-Sierra, E.J. (2005). Evidence from surface tension and fluorescence data of a pyrene-assisted micelle-like assemblage of humic substances. *Water Research*, Vol.39, No.16, pp.3811-3818.

Skopp, J.; Jawson, M.D. & Doran, J.W. (1990). Steady-state aerobic microbial activity as a function of soil water content. *Soil Science Society of America Journal*, Vol.54, No.6, pp.1619-1625

Smolen, J.M. & Stone, A.T. (1998). Metal (hydr)oxide surface-catalyzed hydrolysis of chlorpyrifos-methyl, chlorpyrifos-methyl oxon, and paraoxon. *Soil Science Society of America Journal*, Vol.62, No.3, pp.636-643

Steinberg, S.M.; Pignatello, J.J. & Sawhney, B.L. (1987). Persistence of 1,2-dibromoethane in soils: entrapment in intraparticle micropores. *Environmental Science & Technology*, Vol.21, No.12, pp.1201-1208

Stenrød, M.; Charnay, M.P.; Benoit, P. & Eklo O.M. (2006). Spatial variability in microbial soil characteristics in two sandy loam norvegian soils as affected by surface topographical variability. *Soil Biology & Biochemistry*, Vol.38, No.5, pp.962-971

Strong D.T.; Sale, P.W.G. & Helyar, K.R. (1998). The influence of the soil matrix on nitrogen mineralisation and nitrification. II The pore system as a framework for mapping the

organisation of the soil matrix. *Australian Journal of Soil Research*, Vol.36, No.5, pp.855-872.

Sutton, R. & Sposito, G. (2005). Molecular structure in soil humic substances: the new view. *Environmental Science & Technology*, Vol. 39, No.23, pp.9009-9015

Swann, C.W. & Behrens, R. (1972). Phytotoxicity of trifluralin vapors from soil. *Weed Science*, Vol.20, No.2, pp.143-146

Tajeddine, L.; Nemmaoui, M.; Mountacer, H.; Dahchour, A. & Sarakha, M. (2010). Photodegradation of fenamiphos on the surface of clays and soils. *Environmental Chemistry Letters*, Vol.8, No.2, pp.123-128

Tao, S. & Lu, X. (1999). Estimation of organic carbon normalized sorption coefficient (Koc) for soils by topological indices and polarity factors. *Chemosphere*, Vol.39, No.12, pp.2019-2034

Ten Hulscher, T.E.M. & Cornelissen, G. (1996). Effect of temperature on sorption equilibrium and sorption kinetics of organic micropollutants – A review. *Chemosphere*, Vol.32, No.4, pp.609-626

Tixier, C.; Sancelme, M.; Aït-Aïssa, S.; Widehem, P.; Bonnemoy, F.; Cuer, A.; Truffaut, A. & Veschambre, H. (2002). Biotransformation of phenylurea herbicides by a soil bacterial strain, Arthrobacter sp. N2: structure, ecotoxicity and fate of diuron metabolite with soil fungi. *Chemosphere*, Vol. 46, No., pp.519-526

Van Oss, C.J. (1994). *Interfacial Forces in Aqueous Media*, Marcel Dekker, ISBN 0-8247-9168-1, New-York

Vereecken, H.; Vanderborght, J.; Kasteel, R.; Spiteller, M.; Schäffer, A. & Close, M. (2011). Do lab-derived distribution coefficient values of pesticides match distribution coefficient values determined from column and field-scale experiments? A critical analysis of relevant literature. *Journal of Environmental Quality*, Vol.40, No.3, pp.879-898.

Vieublé-Gonod, L.; Chenu, C. & Soulas, G. (2003). Spatial variability of 2,4-Dichlorophenoxyacetic acid (2,4-D) mineralisation potential at a millimetre scale in soil. *Soil Biology & Biochemistry*, Vol.35, No.3, pp.373-382

Vieublé-Gonod, L.; Chadoeuf, J. & Chenu, C. (2006). Spatial distribution of microbial 2,4-Dichlorophenoxy acetic acid mineralization from field to microhabitat scales. *Soil Science Society of America Journal*, Vol.70, No.1, pp.64-71

Vieublé-Gonod, L.; Benoit, P.; Cohen, N. & Houot, S. (2009). Spatial and temporal heterogeneity of soil microorganisms and isoproturon degrading activity in a tilled soil amended with urban waste composts. *Soil Biology & Biochemistry*, Vol.41, No.12, pp.2558-2567

Vincent, A.; Benoit, P.; Pot, V.; Madrigal, I.; Delgado-Moreno, L. & Labat, C. (2007). Impact of different land uses on the migration of two herbicides in silt loam soil: unsaturated soil column displacement studies. *European Journal of Soil Science*, Vol.58, No.1, pp.320-328

Walker, A. & Jurado-Exposito, M. (1998). Adsorption of isoproturon, diuron and metsulfuron-methyl in two soils at high soil:solution ratios. *Weed Research*, Vol.38, No.4, pp.229-238

Walse, S.S.; Morgan, S.L.; Kong, L. & Ferry, J.L. (2004). Role of dissolved organic matter, nitrate, and bicarbonate in the photolysis of aqueous fipronil. *Environmental Science & Technology*, Vol.38, No.14, pp.3908-3915

Wu, F.; Li, J.; Peng, Z. & Deng, N. (2008). Photochemical formation of hydroxyl radicals catalyzed by montmorillonite. *Chemosphere*, Vol.72, No.3, pp.407–413

Xiaozhen, F.; Bo, L. & Gong, A. (2005). Dynamics of solar light photodegradation behavior of atrazine on soil surface. *Journal of Hazardous Materials*, Vol.117, No.1, pp.75-79

Xing, B.; McGill, W.B. & Dudas, M.J. (1994). Sorption of [alpha]-naphthol onto organic sorbents varying in polarity and aromaticity. *Chemosphere*, Vol.28, No.1, pp.145-153

Xing, B. & Pignatello, J.J. (1997). Dual-mode sorption of low-polarity Compounds in glassy poly(vinyl chloride) and soil organic matter. *Environmental Science & Technology* Vol.31, No.3, pp.792-799

Yuste, Y.C.; Penuelas, J.; Estiarte, M.; Garcia-Mas, J.; Mattana, S.; Ogaya, R.; Pujol, M. & Sardans, J. (2011) Drought-resistant fungi control soil organic matter decomposition and its response to temperature. *Global Change Biology*, Vol.17, No.3, pp.1475-1486

Zhang, H.; Chen, W.R. & Huang, C.H. (2008). Kinetic modeling of oxidation of antibacterial agents by manganese oxide. *Environmental Science & Technology*, Vol.42, No.15, pp.5548–5554

Zhang, H. & Weber, E.J. (2009). Elucidating the role of electron shuttles in reductive transformations in anaerobic sediments. *Environmental Science & Technology*, Vol. 43, No.4, pp.1042–1048

Pesticides in the Modern World - Risks and Benefits

Edited by Dr. Margarita Stoytcheva

This book is a compilation of 29 chapters focused on: pesticides and food production, environmental effects of pesticides, and pesticides mobility, transport and fate. The first book section addresses the benefits of the pest control for crop protection and food supply increasing, and the associated risks of food contamination. The second book section is dedicated to the effects of pesticides on the non-target organisms and the environment such as: effects involving pollinators, effects on nutrient cycling in ecosystems, effects on soil erosion, structure and fertility, effects on water quality, and pesticides resistance development. The third book section furnishes numerous data contributing to the better understanding of the pesticides mobility, transport and fate. The addressed in this book issues should attract the public concern to support rational decisions to pesticides use.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Véronique Chaplain, Laure Mamy, Laure Vieublé-Gonod, Christian Mougin, Pierre Benoit, Enrique Barriuso and Sylvie Nélieu (2011). Fate of Pesticides in Soils: Toward an Integrated Approach of Influential Factors, Pesticides in the Modern World - Risks and Benefits, Dr. Margarita Stoytcheva (Ed.), ISBN: 978-953-307-458-0, InTech, Available from: http://www.intechopen.com/books/pesticides-in-the-modern-world-risks-and-benefits/fate-of-pesticides-in-soils-toward-an-integrated-approach-of-influential-factors

INTECH

open science | open minds