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Sorption of Pesticides on Natural Geosorbents

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1. Introduction

Pesticides are chemicals used to manage pest organisms in both agricultural and non-agricultural environments. They include important classes of compounds such as herbicides, insecticides, fungicides, and biocides (Table 1). Their dispersion into agricultural environments occurs through a variety of methods including air and ground spraying. Relatively few pesticide applications are made directly and exclusively to a target pest, and most application methods rely on the use of an appreciable quantity of pesticides to the environment so that exposure to the pest species reaches effective levels. Estimates for some scenarios indicate that less than 0.1% of the applied materials reach the target pest (Pimentel & Levitan, 1986), the other important fraction of the discharged pesticide is dispersed in the environment. Considering the inherent toxicity and the possible deleterious effects of pesticides, it is of paramount importance to study the pathway and behaviour of excess pesticides released into the environment. Soils and sediments, also called geosorbents, are important sinks for pesticides because of their tremendous quantities and their ability to accumulate, or sorb, large amounts of harmful compounds. How long does a pesticide remain in soils or in sediments depends on how fast it is volatilized, solubilized or degraded, but also on how strongly it is bound by soils or sediment components (Arias-Estevéz et al., 2008).

Increasing amounts of research reveal that sorption is a key process for deciding the ultimate transport, persistence, bioactivity, and risk exposition of organisms to pesticides in the environment. The extent of sorption is related to structural and chemical characteristics of the pesticides (Table 1) that control some environmentally important physicochemical parameters such as volatility, water solubility, and octanol-water partition coefficient. Moreover, various soil or sediment properties including organic matter content, type and amount of clay content, ion exchange capacity and pH also modulate the magnitude of the sorption on geosorbents. A way to describe the subtle interactions of pesticides with natural geosorbents is to discuss their compositions and the interactions involved in the sorption process and the key equations that describe the sorption in an environmental perspective. The main objective of this brief review is to examine the processes of sorption on natural solids, the geosorbents, which strongly determine the persistence, mobility and bioavailability of pesticides in the environment.

2. Sorption phenomenology and terminology

The estimate concentration of atoms or molecules at the surface of condensed phases, solid or liquid, is on the order of 10^{15} molecules/cm² (Somorjai & Li, 2010). When a molecule or an

ion approaches any surfaces, it encounters many attractive forces that eventually will cause its physical adherence or its bonding to the surface of condensed phase. This process in which molecules or ions become associated with solid phases is generally called sorption. Therefore, sorption is a generic term that designates all the relevant processes, which are involved when a pesticide comes into contact with solid matrices, without reference to a specific mechanism. The surface of the material where the sorption occurs is called substrate or sorbent and the chemical that interacts with the sorbent is the sorbate.

Chemical characteristics	Examples	Effects
Ionic		
Cationic	Diquat, paraquat	Herbicide
Basic	Atrazine, simazine	Herbicide
Acidic	Dicamba, MCPA,	Herbicide
Miscellaneous	Bromacil	Herbicide
Nonionic		
Chlorinated hydrocarbons	Lindane, DDT, Toxaphene	Insecticide
Organophosphorous	Methyl parathion, diazinon	Insecticide, fungicide
Dinitroanilides	Trifluralin, oryzalin	Herbicide
Carbanilates	Chlorpropham, barban	Herbicide
Benzonitriles	Dichlobenil	Herbicide
Acetamides	Allidochlor	Herbicide
Carbothioates	Molinate	Herbicide
Thiocarbamates	Triallate, cycloate	Herbicide, fungicide
Anilides	Alachlor, propanil	Herbicide, fungicide
Ureas	Linuron, diuron	Herbicide, algicide
Methylcarbamates	Carbaryl, terbutol	Insecticide

Table 1. Classification of pesticides according to chemical properties (modified from Gevaio et al., 2000)

In the environment, the natural sorbents, called geosorbents, are soils, aquifer solids, suspended particulate matter or sediments. Geosorbents, shown in Figure 1, are very heterogeneous at various particle, aggregate and sample scales which vary temporally as well as spatially (Luthy et al., 1997, Bronick & Lal, 2005, Ehlers & Loibner, 2006). If the process of sorption occurs onto a two-dimensional surface it is called adsorption. It is always an exothermic process where geosorbent-adsorbate bonds (see section 4) are usually stronger than the bonds between adsorbed chemicals (Somorjai & Li, 2010). Those interactions conduct to the formation of a layer of adsorbate retained at the surface of the geosorbent where it is difficult to remove the sorbate. If the molecule, instead of residing at the surface of the geosorbent, penetrates into the three-dimensional matrix or into the pores in the solid, the process is called absorption.

3. Geosorbent composition

Structural and molecular compositions of geosorbents have a direct control on the sorption and retention of pesticides. As shown in Figure 1, geosorbents are primarily formed by a complex assemblage of inorganic minerals and natural organic matter. These two types of material are free or associated to form macro- and microaggregates with size distribution and inter- and intra-aggregate pore continuity (Luthy et al., 1997, Six et al., 2004, Bronick & Lal, 2005, Jasinka et al., 2006, Kögel-Knabner et al., 2008). The macropores (pore size larger than 50 nm), mesopores (pore size between 2 and 50 nm) and micropores (pore size smaller than 2 nm) limit more or less the advective and diffusive transport of the contaminant into the geosorbents. The transport of pollutants at the surface of a geosorbent or inside its core allows them to reach potential sorption domains or sites of the most reactive surfaces. The pores increase the surface where pesticides can interact with the geosorbents. For pesticides with low polarity and slight solubility in water, e.i. in the mg liter⁻¹ range or less, organic matter surface of the geosorbent is the principal domain where sorption occurs (Wauchope et al., 2002). However, when organic carbon content of the geosorbent becomes relatively low (<0.1 %), other reactive surfaces can favor the sorption of pesticides (Wauchope et al., 2002, Ehlers & Loibner, 2006, Kah & Brown, 2006). Among the inorganic surfaces present in the geosorbents, the clay minerals and sesquioxides (oxides, hydroxides and oxyhydroxides of Al and Fe) have been reported to significantly contribute to the sorption of pesticides (Luthy et al., 1997, Wauchope et al., 2002, Ehlers & Loibner, 2006, Kah & Brown, 2006). Therefore, the sorption capacity of a geosorbent for pesticides is dependant of the clay minerals, Fe- and Al-oxide contents as well as organic matter content and its composition.

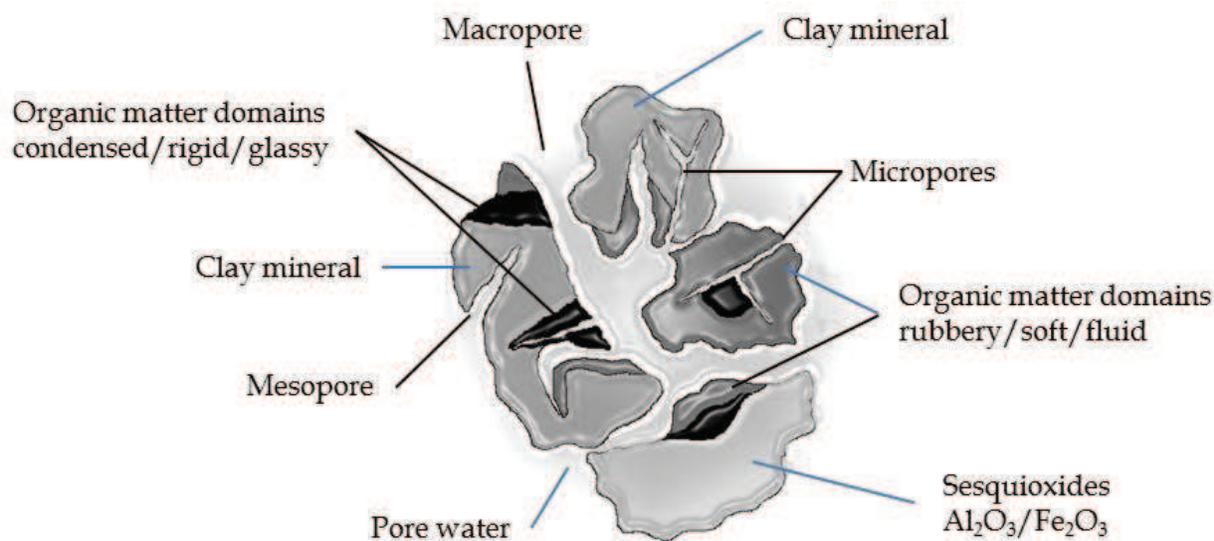


Fig. 1. Simple schematic of a geosorbent particule aggregate showing inorganic and organic materials and different porosities.

4. Interactions between chemicals and geosorbents

The type of interaction between a chemical and a geosorbent reactive surface depends on the nature of the organic and inorganic matter as well as chemical moieties present in the

chemical. Weber et al. (1991) summarize the interactions in three categories: physical, chemical and electrostatic. The physical sorption invokes weak van der Waals interactions and entropy changes. Chemical interactions include hydrogen bonds and covalent bonds, whereas electrostatic interactions involve ion-ion and ion-dipole forces. However, during recent years our qualitative understanding of the mechanisms explaining the retention of nonpolar organic compounds and pesticides onto organic matter and clays has been considerably refined (Senesi, 1992, Pignatello & Xing, 1996, Luthy et al., 1997, Gevaio et al., 2000, Cornelissen et al., 2005, Lagaly, 2001, Huang et al., 2003, Calvet et al., 2005, Kah & Brown, 2006, Cornejo et al., 2008, Keiluweit & Kleber, 2009). The interactions responsible for the retention of pesticides on geosorbents are briefly summarized here.

Weak van der Waals attractions between sorbate and geosorbent molecules are mediated by permanent or induced electric dipoles present in the chemicals when molecules come as close as possible together. These slight dispersive interactions (London, Debye and Keesom forces) are short-range attractions but are present in the sorption processes of all chemical compounds. Moreover, for nonionic pesticides, these forces play a master role in the sorption mechanism and they are often greatly amplified in voluminous nonpolar hydrophobic molecules which are easily polarizable. They can also play a very important role when many molecules in a supramolecular structure like humic aggregates interact simultaneously (Sposito, 2008). This mechanism have been proposed to contribute to the sorption of many pesticides such as atrazine (Barriuso et al., 1994, Konstantinou & Albanis, 2000), imazethapyr (Senesi et al., 1997), fluridone (Weber et al., 1986), methomyl (Yang et al., 2005), isoproturon (Worrall et al., 1996), carbaryl and parathion (Lenheer & Aldrichs, 1971), simazine (Celis et al., 1997), methamidophos (Yu & Zhou, 2005), and 2,4-dichlorophenoxyacetic acid (Calvet, 1989).

Hydrophobic interactions are not a two-body interaction like the van der Waals interactions. They are rather a thermodynamic force which tends to minimize the interfacial area between hydrophobic solutes and a hydrophilic solvent (Somorjai & Li, 2010). Pesticides molecules are often made from hydrophobic moieties. If these moieties can approach close to the organic surface of the geosorbents, some attractive interactions will develop near the surface. These interactions occur from enthalpy and entropy changes associated with water-water, nonionic compound-water, and geosorbent-water interactions, as well as from van der Waals forces between nonpolar moieties of the chemical and some sorption sites in the geosorbent (Chiou et al., 1979, Karickhoff, 1984, Lagaly, 2001, Keiluweit & Kleber, 2009, Schwarzenbach et al., 1993). Active sites on geosorbents include aliphatic side chains or lipid portions and lignin-derived aromatic moieties present in humic substances (Senesi, 1992, Chefetz & Xing, 2009, Mao et al., 2007). Humic substances are the most important class of molecules present in the natural organic matter (Thurman, 1985, Senesi, 1992, Tremblay & Gagné, 2009). Hydrophobic interactions are proposed as an important mechanism for the sorption of many pesticides such as DDT, endrin and other organochlorine pesticides (Lenheer & Aldrichs, 1971, Peng et al., 2009), atrazine and simazine (Herwig et al., 2001), 2,4-dichlorophenoxyacetic acid and triclopyr (Johnson et al., 1995), imazaquin (Ferreira et al., 2002), carbaryl (de Oliveira et al., 2005), pentachlorophenol (Lee et al., 1990), primisulfuron (Ukrainczyk & Ajwa, 1996), prometryn (Khan, 1982), s-triazine herbicides (Celis et al., 1997) and imidacloprid (Liu et al., 2006).

The presence of numerous polar oxygen and hydroxyl-containing groups in pesticides, humic substances or clays gives rise to the formation of hydrogen bonds between electron-

withdrawing atoms (F, Cl, N and O) and electropositive hydrogen nucleus of functional groups such as -OH, NH, Si-OH or Al-OH. This type of chemical interaction is usually stronger than van der Waals interactions. Evidence of hydrogen bonding between pesticides and geosorbents are reported for many pesticides such as methomyl (Cox et al., 1993, Yang et al., 2005), primisulfuron (Pusino et al., 2004), glyphosate (Vereecken, 2005), 2,4-dichlorophenoxyacetic acid (Hyun & Lee, 2005), and atrazine (Martin-Neto et al., 1994, Kovaioš et al., 2006, Lima et al., 2010).

A charge-transfer complex or electron-donor-acceptor (EDA) complex is an association of two or more molecules, or of different parts of one very large molecule, in which a fraction of electronic charge is transferred between the molecular entities (Anonymous, 2010). The electrostatic interaction supplies the stabilizing force for the formation of a molecular complex. The source molecules from which the charge are transferred are called the electron donors and the receiving species are called the electron acceptors. In the case of aromatic systems, electron-rich aromatic π -systems can act as π -donors, and electron-deficient π -systems as π -acceptors. As a consequence of the charge associated with π -systems, EDA interactions occur between both π -donors and π -acceptors with entities possessing the complementary property (electron-deficient or electron-rich, respectively). These entities include polarized and charged mineral surface sites, functional groups, and aromatic π -systems (Keiluweit & Kleber, 2009). The presence in humic substances of both electron rich moieties, such as diphenols, and electron-deficient structures, such as quinines, suggests the possible formation of π - π EDA charge transfer complexes with pesticides. Pesticides can act as electron donors (amine and/or heterocyclic nitrogen atom of the s-triazines, pyridines, imidazoles) or electron acceptors (e.g. deactivated bipyridilium ring of atrazine) (Senesi, 1992). An EDA mechanism between atrazine and soil organic matter has been postulated but the mechanisms are still a controversy (Martin-Neto et al., 1994, Welhouse & Bleam, 1993, Martin-Neto et al., 2001, Celano et al., 2008). EDA interactions between aromatic ring in trifluralin and soils aromatics seem possible but are likely to be weak (Shirzadi et al., 2008).

Adsorption by a ligand-exchange mechanism involves the replacement, by suitable adsorbent molecules such as s-triazines and anionic pesticides, of hydration water or other relatively weak ligands that partially hold polyvalent cations associated to soil organic matter or hydrous oxide surface (Senesi, 1992). The substitution may be facilitated by an entropy change, if an adsorbate molecule succeeds in replacing several water molecules associated with one or several complexed metal ion(s) (Gevao et al., 2000). As reviewed by Ainsworth et al. (1993), a two-step reaction mechanism is possible for ligand exchange at oxide surfaces. The first reaction involves the rapid formation of an ion-pair complex on the protonated surface site (outer-sphere complex), and the second reaction, rate limiting, involves the breaking and forming of bonds (Zhang & Sparks, 1989) and results in the formation of an inner-sphere complex that may be bidentate or binuclear (Ainsworth et al., 1993). The ligand-exchange mechanism is involved in the retention of many organic acids to oxide surfaces: for example an organic functional group, such as carboxylate or hydroxyl, displaces a surface coordinated -OH or water molecule of a metal ion (Fe, Al) at the surface of a soil mineral. The ligand exchange mechanism is proposed as a mechanism of retention of pesticide on geosorbents for clofenset (Dubus et al., 2001), 2,4-dichlorophenoxyacetic acid (Hiradate et al., 2007), azimsulfuron (Pinna et al., 2004, Kah & Brown, 2006), pentachlorophenol (Hyun et al., 2003) and for zwitterionic compounds such as imazaquin on highly weathered tropical soils (Regitano et al., 2000).

Pesticides sorbed by ion exchange or ionic bonding exist as cations or anions in solution or are pesticides that can be protonated or dissociated under current pH conditions in the environment. The ion exchange process occurs when an ionized pesticide in solution is exchanged for a similarly charged ion attached to an opposite charge, which is itself bonded to geosorbents (similar to ion exchange chromatography). It must be emphasized that ionic interactions between pesticides and geosorbents are always accompanied by van der Waals interactions and usually, also with polar interactions. However, electrostatic interactions between opposite charges are stronger than other attractions and they dominate the interactions with the geosorbents.

Geosorbents present good surfaces for ion exchange processes with pesticides. Under temperate regions, the predominant minerals in the clay fraction of the soils are aluminosilicates in form of sandwiches of tetrahedral and octahedral sheet structures bearing negative charges (Sposito, 1989, Cornejo et al., 2008). These charges are compensated by exchangeable hydrated inorganic cations. Pesticides, in a cationic form, such as chlordimeform, diquat, paraquat and difenzoquat can substitute to inorganic cations at the clay mineral geosorbent surface by cation-exchange processes (Weber & Weed, 1968, Rytwo et al., 2004). Cation exchange is also relevant for triazines (Sannino et al., 1999, Herwig et al., 2001) even though their pKa is lower than the pH of common soils (Kah & Brown, 2006). Sannino et al. (1999) studying the interaction of pesticides with $Al(OH)_x$ clay complexes have suggested that simazine molecules arrive at support interfaces mostly as molecular species. Then, the molecules dissociated as cations by the microenvironmental pH are eventually adsorbed by cation exchange. Cation exchange can also occur between the protonated triazines or the positively charged bipyridylium compounds (e.g., diquat or paraquat) and the negatively charged sites of humic substances (carboxylate, phenolate groups) (Senesi et al., 1995). However, not all negative sites on the organic matter are available to bind with large organic cations, some steric hindrance factor could occur. For instance, the higher reactivity of simazine relative to atrazine and prometryn may be related to the smaller steric hindrance of the reactive N-H group of the former herbicide (Senesi, 1992).

Adsorption of pesticide anions via anion exchange is an unfavorable process under temperate climates where clays and soil organic matter are generally either noncharged or negatively charged (EPA, 1999). Moreover, direct sorption involving the few positive charges at the edge of sheets in clays or protonated amine groups within the organic matter is an insignificant mechanism for weak acids (Stevenson, 1972, Kah & Brown, 2006, Cornejo et al., 2008). Under tropical and subtropical regions, the hydrated oxides of iron and aluminum are largely present bearing positive charges (EPA, 1999, Hillel, 2004, Sposito, 1989) where anion exchange is likely to occur at the surface of geosorbents. Anion exchange was implicated in the adsorption of the dissociated form of chlorsulfuron (Shea, 1986), 2,4-dichlorophenoxyacetic acid (Dubus et al., 2001, Watson et al., 1973), mecoprop and bentazone (Clausen et al., 2001), and clofenset (Dubus et al., 2001). Because anion exchange is affected by the presence of other anions, Hyun et al. (2003) suggest that sorption of acidic pesticides could be better predicted by considering the electrolyte composition.

5. Quantitative description of the sorption

Following Azizian (2004), to properly understand the sorption process, we must appreciate two fundamental aspects: equilibria and kinetics. Equilibria deal with thermodynamic data

that only provide quantitative information about the difference between the initial and final states of a system. In contrast, kinetics deals with changes in chemical properties in time and is concerned especially with rates of changes (Azizian, 2004). The sorption kinetics is of interest for many aspects of pesticides chemistry. It allows exploring adsorption /desorption mechanisms, the removal of pesticides from solutions by natural or synthetic geosorbents or the mobility of pesticides in soil columns.

Ho et al. (2000) and Plazinski et al. (2009) have suggested that the sorption process affecting any pollutants can be described by four consecutive steps. Adapted to pesticides these steps are: (i) transport of the pesticide in the bulk of the solution; (ii) diffusion of the pesticide across the liquid film surrounding the geosorbent particles; (iii) diffusion of pesticide in the liquid contained in the pores of geosorbents and along the pore walls (intraparticle diffusion); and (iv) adsorption and desorption of pesticide molecule on and from geosorbent surfaces or sorption domains. One of the previous steps or any combination of these four steps may be the rate limiting factor that controls the overall sorption rate. Thus, the sorption of pesticides could be under the control of physical processes (transport and diffusion of the pesticide to the liquid/solid interface or dependent on the intensity of the van der Waals forces) or could be under some chemical controls (strong chemical interactions). Even if in many experimental sorption systems a rapid mechanical mixing eliminates the effect of transport in the solution so that it does not become rate limiting, it is difficult to quantitatively determine the contribution of the other steps in the sorption process.

We have discussed the nature of the interactions responsible for the sorption or retention of pesticides onto geosorbents. However, currently, there are no direct observational data revealing the molecular-scale location in which pollutant molecules accumulate when associated with geosorbents (Luthy et al., 1997). Then, macroscopic observations are mandatory to make inferences about the sorption mechanisms. Luthy et al. (1997) reviewed the sequestration of hydrophobic organic contaminants by geosorbents. Considering the kinetics of sorption (fast or slow), the isotherm form (linear or not), the activation energy and the heat of sorption, the competition for sorption domain, the steric hindrance associated to sorbate and the solvent extractability, they proposed to group sorption data into five qualitative cases that may be useful to assess sorption mechanism of nonpolar organic compounds. These cases are : i) absorption into amorphous or "soft" natural organic matter or entrapped nonaqueous-phase liquids (solvents, oils and tars); ii) absorption into condensed or "hard" organic polymeric matter or combustion residues (e.g. soot); iii) adsorption onto water-wet organic surfaces (e.g. soot); iv) adsorption to exposed water-wet mineral surfaces (e.g. quartz); and v) adsorption into microvoids or microporous minerals (e.g. Zeolites) with porous surfaces at water saturation <100%. Although useful to discuss the sorption, this classification is limited to hydrophobic pesticides and does not cover all the pesticides. Moreover, this categorization is only qualitative.

The interactions of pesticides with a geosorbent are a very complex process where different forces and interactions are involved for various periods of time. Moreover, climatic factors such as temperature, sunlight, and rainfall/run-off as well as biotic factors such as microbial degradation of pesticides affect local conditions where sorption occurs. Therefore it is difficult to isolate and to quantify a specific mechanism of sorption because of the myriad of variables and the variety of processes that are likely to contribute or to trigger the sorption at the molecular scale in the environment. Thus, to know the magnitude of the sorption of a

pesticide in a soil we must use an empirical approach. Under laboratory controlled conditions it is possible to estimate the extent of all the interactions committed in the sorption or desorption process by the measurement of a sorption coefficient, K^S_d , or a desorption coefficient, K^D_d . These sorption coefficients are specific to a pesticide/geosorbent system and are useful for comparative and modeling purposes.

Delle Site (2001) identified and reviewed fifteen experimental methods and seven prediction methods for the determination and estimation of the sorption coefficients of organic compounds in natural sorbent/water systems. The most common method to study the sorption/desorption process is however the batch equilibrium method (EPA, 1999, OECD, 2000, Wauchope et al., 2002). In this method, a known mass of geosorbent (soil, sediment or suspended matter) is introduced into a vial (a batch reactor) and is conditioned in a known volume of appropriate liquid matrix (distilled water or water containing electrolytes (NaCl, CaCl₂, or sea salts)). A known volume of solution (in the appropriate matrix) of the pesticide at known concentration is added to the slurry. A minimum headspace is left to avoid losses of solute in vapour phase. The vial is then mixed gently for a specified period of time suitable to reach equilibrium, typically from 2 to 48h, 24h being usual (Wauchope et al., 2002). At the end of the agitation period, the solid is separated from the solution and the concentration of the pesticide remaining in solution is measured. The amount of pesticide sorbed on the geosorbent sample is obtained by the difference between the amount of pesticide, introduced in the batch reactor and the amount remaining in the solution at the end of experiment. The amount of sorbed substance can also be measured by the direct extraction of the geosorbent. This procedure is however more tedious than analysing the aqueous phase. Desorption studies could also be operated after the adsorption step. In the desorption assay, a specific volume of supernatant is removed for analysis, and is replaced by the same volume of the appropriate liquid matrix. The sample is shaken, centrifuged and the supernatant analyzed to complete the first cycle. At least two further decant/refill desorption cycles should be completed to generate acceptable desorption data (Bowman, 1979, Agriculture Canada, 1987, OECD, 2000).

Batch sorption measurements present few disadvantages (Delle Site, 2001, EPA, 1999, Strandberg & Fortkamp, 2005, Soubaneh et al., 2008). Losses of chemicals by volatilization and by biological or chemical degradation are possible, and the length of the experiment could be insufficient to reach equilibrium; also the complete separation between geosorbent and the water phase is difficult. Another important point reported for selected inorganic substances (EPA, 2004) is that a batch sorption test does not necessarily reproduce the chemical reaction conditions that take place in the real environment. For instance, in a soil column, water percolates through it at a finite rate and both reaction time and degree of mixing between water and soil can be much less than those occurring in a laboratory batch test. Consequently, K^S_d values obtained from batch experiments can be different than those in a real system. Another disadvantage is that they do not accurately simulate desorption of the contaminants from a contaminated soil because it is often hypothesized that sorption and desorption reactions are reversible and K^S_d and K^D_d values are the same (EPA, 2004). This assumption is contrary to many observations that show that the sorption/desorption equilibrium may not be fully reversible, a phenomenon called hysteresis (Delle Site, 2001 and references therein, Wauchope et al., 2002).

Even though the drawbacks of the batch sorption technique are multiple, the method presents numerous advantages (Strandberg & Fortkamp, 2005). The assay is inexpensive,

there is no requirement for complex or extra equipment in the lab, the methodology is quite simple and the tests can be done in few days. Therefore, it allows studying the sorption of harmful substances under a wide variety of environmental conditions relatively quickly. Last but not least, this method is so commonly used that it facilitates the comparison with results from other studies.

6. Sorption equilibrium models

The equilibrium exchange of pesticides between the aqueous phase and a geosorbent, such as soils, aquifer solids, suspended particulate matter or sediments, is quantified by the geosorbent/solution sorption distribution coefficient, K_d^s , which is defined as the ratio between the concentration of the pesticide in the geosorbent phase (C_s) and its concentration in the solution (C_e). As shown in equation 1, the sorption distribution coefficient corresponds also to the ratio of the amount of pesticide (Q_s) fixed on the solid phase (M) to the amount of pesticide freely dissolved (Q_e) in the volume of aqueous phase (V).

$$K_d^s = \frac{C_s}{C_e} = \frac{Q_s/M}{Q_e/V} \quad (1)$$

In many cases, the sorption distribution coefficient of non-polar pesticides and the fraction (%) of organic carbon content (f_{oc}) in geosorbents are correlated (Weber et al., 2000, Wauchope et al., 2002). This correlation means that pesticides have a preferential affinity to bind with organic matter instead of minerals present in the geosorbents. Thus, a carbon-normalised sorption coefficient, K_{oc} , allows comparison among pesticide sorption affinities for geosorbents with different amount of organic matter. The K_{oc} parameter can be calculated from equation 2. K_{oc} values are universally used as a measure of the relative

$$K_{oc} = \frac{K_d^s}{f_{oc}} \quad (2)$$

potential mobility of hydrophobic pesticides in soils (Wauchope et al., 2002). High values of K_{oc} suggest that pesticides could be considered as immobile in soils or sediments (McCall et al., 1980) and the low values caution a high leaching risk.

It seems easy to measure K_d^s from equation 1. In fact, the determination of the quantity of pesticide in the aqueous or solid phase of batch sorption experiments may be associated with difficulties if the pesticide is liquid-liquid extracted with an organic solvent. For instance, pesticide can be lost during the evaporation treatments used to concentrate the analyte. In addition, loss of pesticide may also occur by its adsorption onto the glass walls, stir bar or Teflon caps of the material used. This phenomenon is expected since many other nonpolar organic compounds in aqueous solutions have strong affinities for glass and Teflon-coating parts (Baltussen et al., 1999; Ackerman & Hurtubise, 2000). Loss of pesticide may also happen by degradation in the reactor as reported for few toxaphene congeners (Lacayor et al., 2004). As clearly shown by Soubaneh et al. (2008), the evaluation and correction of these potential losses will improve the determination of the distribution coefficient values.

It is important to recall that empirical K_d measured in the batch sorption experiments represent an integration of all sorptive processes occurring in the batch sorption reactor as illustrated in Figure 2, where the toxaphene pesticide is used as a model compound. In the

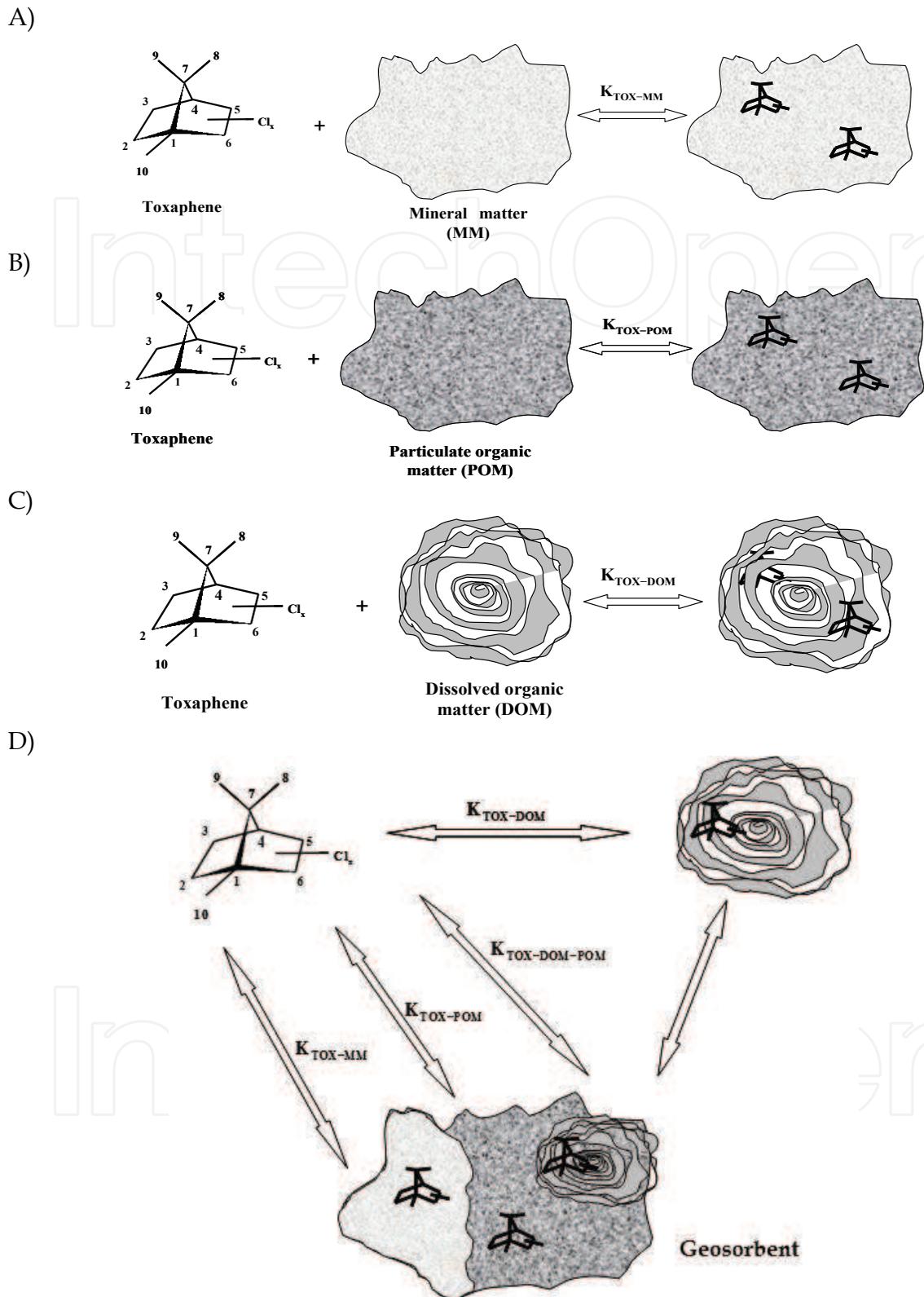


Fig. 2. Possible interactions of toxaphene pesticide with geosorbents. a) sorption of toxaphene on mineral surface ($K_{\text{TOX-MM}}$); b) sorption of toxaphene on particulate organic matter surface ($K_{\text{TOX-POM}}$); c) interactions of toxaphene with dissolved organic matter ($K_{\text{TOX-DOM}}$); d) sorption of toxaphene on natural geosorbent.

reactor, the mixing of the toxaphene with a geosorbant is done until equilibrium is reached (Fig 2d). This equilibrium is complex since competitive equilibria occur between the pesticide and mineral phases (Fig 2a), the pesticide and the particulate organic material (Fig 2 b) and the pesticide with the dissolved organic matter (Fig 2c) present in the environment of the geosorbent. Moreover, the pesticide-dissolved organic matter complex can sorb to the geosorbant (to organic and mineral phases). Each of these equilibria possesses its own distribution coefficient identified by $K_{\text{TOX-MM}}$, $K_{\text{TOX-POM}}$, $K_{\text{TOX-DOM}}$, $K_{\text{TOX-DOM-POM}}$ and $K_{\text{TOX-DOM-MM}}$ (not shown) in Figure 2. In practice, the equilibrium between dissolved organic matter and the pesticide is difficult to quantify and need further studies. However a correction for this effect is frequently neglected in the evaluation of K_d . Nevertheless, in equation 1, C_e refers to the concentration of the freely dissolved molecules of pesticide rather than to the total concentration in the soil solution, which might contain fractions that are sorbed to colloidal particles or to dissolved organic matter. Spark and Swift (2002) have suggested that dissolved organic matter have a negligible effect on the sorption characteristic of atrazine, isoproturon and 2,4-dichlorophenoxyacetic acid. However, if a soil solution contains high concentrations of dissolved organic matter there is a possibility that the dissolved organic might facilitate the transport of pesticides through the soils.

A batch sorption experiment gives a sorption coefficient that is only valid for a particular geosorbent and for the aqueous conditions of the experiment (pesticide concentration, solution matrix, temperature). Thus, the constant K_s^D does not address the sensitivity of the sorption to changing conditions that occur in environment. More useful is a series of batch sorption experiments done at multiple concentrations. The results of these assays permit the generation of sorption isotherms from which the dependence of K_s^D on C_e can be determined. OECD (2000) has suggested using five concentrations covering preferably two orders of magnitude to construct isotherms. Weber et al. (2000) suggested that concentrations used to construct sorption isotherms may range from 0.1 to 100 nmol mL⁻¹. Several sorption models have been developed to describe, quantify and explain the sorptive process of pesticides on geosorbents. The simplest one is the linear model depicted by the equation 3 used to formulate sorption/desorption isotherms. This equation is simply the equation 1 reformulated to incorporate K_s^D , the sorption or desorption coefficient.

$$C_s = K_s^D C_e \quad (3)$$

This linear model is adequate if the sorption sites are of the same nature and in great amount to accommodate the chemical as the concentration increases. As shown in Figures 1 and 2, the heterogeneity of the geosorbents is real and deviations from the linear sorption model are predictable and are effectively observed for pesticides (Delle Site 2001, Wauchope et al., 2002). Two other sorption isotherm models, the Freundlich and Langmuir models, are frequently used when the amount of contaminant retained by the geosorbent is abundant enough to impact the linear sorption.

The Freundlich isotherm is given by equation 4 which can be transformed to a linear equation by making a log-log transformation of the data. In the equation, K_f is the Freundlich sorption coefficient, n is a linearity parameter and C_s and C_e are as described

$$C_s = K_f C_e^n \quad \text{or} \quad \log C_s = \log K_f + n \log C_e \quad (4)$$

previously. When $\log C_s$ is plotted against $\log C_e$, the best-fit straight line has $\log K_f$ as its intercept and a slope of n , an indicator of site energy heterogeneity of the geosorbents. The

values of n are generally comprised between 0.7 and 1.2 (von Oepen et al., 1991, Wauchope et al., 2002). Value of $n = 1$ occurs when all the sorption domains behave in a similar way. When $n = 1$, K_f is equivalent to K_d irrespectively of the concentration C_e and the system performs like the linear model. If $n \neq 1$, K_f and K_d cannot be compared because each constant has its own unit that are different.

Sorption isotherm data could also be fitted to the Langmuir model given by equation 5, with the assumption that geosorbents have a finite number of sorption sites of uniform energy.

$$C_s = \frac{C_{s,max} K_L C_e}{1 + K_L C_e} \quad (5)$$

In equation 5, $C_{s,max}$ designates the maximal sorption capacity and K_L is the Langmuir sorption coefficient related to the energy of sorption. C_s and C_e have the same meaning as previously. Please note that if $K_L C_e$ is high (e.g., at relatively high C_e), C_s approaches $C_{s,max}$ and gives the maximum sorbate capacity of the geosorbent while, for sufficiently small values of C_e ($K_L C_e$ near zero), C_s is linearly related to C_e and $C_{s,max} K_L$ equals K_d the sorption coefficient.

The examination of the form of the isotherm curves for sorption and desorption for the same chemical in a pesticide/geosorbent system is interesting. Under apparent equilibrium conditions, different curves can be obtained for sorption and desorption. In this phenomenon, called hysteresis, the distribution coefficient K^D_d for desorption can be greater than the K^S_d measured for the sorption at a constant C_e concentration (Huang et al, 2003). Experimental artifacts in the desorption experiment may result in the hysteresis (Bowman & Sans, 1985, Huang et al., 1998, Delle Siete, 2001, Calvet et al., 2005). Huang et al. (1998) have suggested, under rigorously controlled experiments, to characterize this hysteresis phenomenon by an hysteresis index defined in equation 6 where C_s^S and C_s^D are the sediment sorbate concentrations for the sorption and single-cycle desorption experiments, respectively. Parameters T and C_e refer to the conditions of constant temperature and constant aqueous phase concentration.

$$\text{Hysteresis Index (HI)} = \frac{C_s^D - C_s^S}{C_s^S} \Bigg|_{T, C_e} \quad (6)$$

The higher the value of HI is, the stronger the sediment will sequester the chemical. A zero HI value indicates that the hysteresis is insignificant and the sorption is reversible.

7. Conclusion

It is of paramount importance to understand the behaviour and fate of excess pesticides released into the environment which is strongly influenced by the interactions between the pesticides and natural solids called geosorbents. The chemical composition of the pesticides and the physical and chemical complexities of the geosorbents modulate the diversity and the intensities of interactions between the pesticides and geosorbents resulting in various destinies for pesticides in the fields. Even though our understanding of the pesticide/geosorbent interactions is mostly qualitative, and that it is difficult to examine the sorption processes at the molecular scale, we have some simple experimental approaches to

quantitatively characterize the sorption phenomenon. The simple batch sorption experiment allows the measurement of a sorption distribution coefficient under near realistic field conditions at a specific concentration of pesticide. However, this datum is of limited interest considering its high specificity. For non-polar pesticides, if the coefficient is normalized for the organic content of the geosorbent, this allows discriminating the affinities of pesticides for various soils or sediments and can be used to evaluate the potential mobility of pesticides in the environment. Batch sorption experiments at different concentrations of a given pesticide provide isotherm curves that are more realistic of the variation in the distribution coefficients in the fields. Close examination of the sorption and desorption isotherms permits some insights into the mechanism of sorption and can also provide a useful hysteresis index to discuss the reversibility of the sorption and the persistence of the pesticides in the environment.

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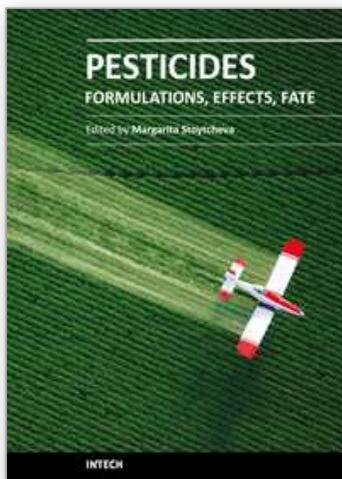
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This book provides an overview on a large variety of pesticide-related topics, organized in three sections. The first part is dedicated to the "safer" pesticides derived from natural materials, the design and the optimization of pesticides formulations, and the techniques for pesticides application. The second part is intended to demonstrate the agricultural products, environmental and biota pesticides contamination and the impacts of the pesticides presence on the ecosystems. The third part presents current investigations of the naturally occurring pesticides degradation phenomena, the environmental effects of the break down products, and different approaches to pesticides residues treatment. Written by leading experts in their respective areas, the book is highly recommended to the professionals, interested in pesticides issues.

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