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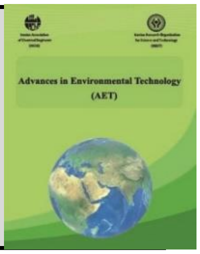

Sorption, degradation and leaching of pesticides in soils amended with organic matter: A review

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ABSTRACT

The use of pesticides in modern agriculture is unavoidable because they are required to control weeds. Pesticides are poisonous; hence, they are dangerous if misused. Understanding the fate of pesticides will be useful to use them safely. Therefore, contaminations of water and soil resources could be avoided. The fates of pesticides in soils are influenced by their sorption, decomposition and movement. Degradation and leaching of pesticides are control by sorption. Soil organic matter and clay content are main soil constituents that have a high capacity for sorption of pesticides. Addition of organic maters to amend the soils is a usual practice that every year has been done in a huge area of worldwide. The added organic amendments to the soils affect the fate of pesticides in soils as well. Pesticides fates in different soils are different. The addition of organic matter to soils causes different fates for pesticides as well. It is known from the studies that sorption of non-ionic pesticides by soil in aqueous system is controlled mainly by the organic matter content of the soils. Sorption of pesticides has been reported to increase by amending soils with organic matter. In general, conditions that promote microbial activity enhance the rate of pesticides degradation, and those that inhibit the growth of microorganisms reduce the rate of degradation. Amendment of soils with organic matter may modify leaching of pesticides in soil. Some studies showed that organic matter added to soils reduced pesticides in ground water. Generally, organic amendments induces the restriction of pesticides leaching in soils.

1. Introduction

The use of pesticides in modern agriculture is unavoidable because they are required to control weeds to ensure adequate food supply. Pesticides are poisonous; hence, they may be dangerous if misused. Understanding the pesticides and soils properties as well as the environmental conditions will help us to apply the pesticides properly. Therefore, contaminations of water and soil resources could be avoided. The fates of pesticides in soils are influenced by their sorption, decomposition and movement [1-3].The rate and amount of pesticides sorbed, degraded and leached in soil depend on the soil and pesticides properties [4,5].The sorption process influences the magnitude of the other processes and is considered to be one of the major processes affecting the interactions occurring between pesticide and the solid phase in the soil environment [6,7]. The main constituents of solid phase are clay minerals, organic matter, oxides and hydroxides of aluminum and iron [8]. Dissipation of pesticides can occur by decomposition, leaching, runoff and volatilization [9-11]. The objective of this review is to present a summary of the reported studies on sorption, degradation and leaching of pesticides in soils, with emphasis on soils amended with organic matter.

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1.1. Definition of sorption

Sorption, degradation and leaching potential of pesticides in soils are major factors that affect the fates of pesticides in soils [1] Sorption is the term used to describe adsorption and /or absorption when the mechanisms and nature of the process is not clear [12]. Adsorption describes the process where constituents are concentrated at the interface of two phases, either the solid-liquid, gaseous-liquid or gaseous-solid boundary. On the other hand, absorption describes the process when a component is transferred from the bulk state of one phase into the bulk state of other phase [8].

1.2. Mechanisms of sorption

Several mechanisms have been proposed to explain adsorption of pesticides by soil constituents. Several mechanisms may occur simultaneously depending on the nature of the pesticides and soil constituents. The main mechanisms for adsorption of pesticides by soils constituents are as following:

1.2.1. Van der Waals attraction

Van der Waals attraction involves the adsorption of nonionic and non-polar pesticides to the nonionic and nonpolar soil moieties. Van der Waals forces result from short-range dipole-dipole interactions of several kinds. The Van der Waals forces between the molecules of adsorbate and adsorbent may result in considerable attraction for the large molecules [13]. The adsorption of carbaryl and parathion on soil organic matter in aqueous media is considered to involve Van der Waals bond between the hydrophobic portions of the adsorbate molecules and the adsorbent surface (De Oliveria et al., 2005).Most of the pesticides may be sorbed to soils through hydrogen bonds and Vander Waals forces [8].

1.2.2. Hydrophobic bonding

Non-polar pesticides that they have significant non-polar regions size are adsorbed onto the hydrophobic regions of soil organic matter [8]. In this case, water molecules present in the system will not compete with the non-polar pesticides for adsorption on hydrophobic regions [14]. Lipids area constituent of soil organic matter and therefore, they are the main sites for adsorption of chlorinated hydrocarbon pesticides. Association between non-polar pesticides including chlorinated hydrocarbons with the lipid fraction of soil organic matter might be described by hydrophobic bonding [14]. Hydrophobic bonding also explains why sorption of certain pesticides is independent on soil water content, especially in soils with high organic matter content. The hydrophobic fraction of peats which includes fats, waxes and resins is a significant adsorbent of phenylureas [14]. The adsorption of pesticides by hydrophobic bonding is also pH independent.

Methylation of organic matter or humic substances to block hydrophilic hydroxyl groups would increase the adsorption by this mechanism. In view of this concept, adsorption of pesticides by a soil can be considered to be primarily a matter of partitioning between organic matter and water. Nonpolar pesticides may be sorbed onto hydrophobic components of soil organic matter through partitioning [15].

1.2.3. Hydrogen bonding

Hydrogen bonding is a kind of interaction in which the hydrogen atom serves as a bridge between two electronegative atoms [16]. Hydrogen bonding is the key mechanism in the adsorption of polar non-ionic molecules on clay minerals [16]. The oxygen containing functional groups and amino groups of organic matter shows that adsorption could occur by the formation of hydrogen bond with polar and non-ionic pesticides containing similar groups [8]. The hydrogen bonding appears to be the most important mechanism for sorption of polar nonionic pesticides on soil organic matter. Carbonyl oxygen group on pesticides molecules may bond to amino hydrogen or hydroxyl functional groups on the soil organic matter [8].

1.2.4. Charge transfer

In the charge transfer mechanism, electrostatic attraction takes place when electrons are transferred from an electron donor to an electron acceptor. The charge transfer formation is especially important in explaining the adsorption of methylthiotriazines onto organic matter [17]. Sadegh-Zadeh et al. (2011) [18] reported that the charge transfer appears to be one of the mechanisms for adsorption of napropamide herbicides on organic portion of soil amended with organic matter.

1.2.5. Ion exchange

Ion exchange is responsible for adsorption of cationic and porotonated pesticides by soils. Adsorption of cationic pesticides including the paraquat and diquat are occurs through carboxylic and phenolic functional groups of soil organic matter [15]. Acidic and protonated-basic pesticides may be sorbed on soil organic matter and minerals via anion exchange mechanism [8].

1.2.6. Ligand exchange

The ligand exchange interaction involves replacement of ligands on the adsorbent by the adsorbed pesticides. This mechanism takes place when the adsorbed pesticides are stronger than the ligands onthe adsorbent which will be replaced [19]. The acidic pesticides may be adsorbed on Al and Fe hydroxides through ligand exchange.

1.3. Sorption isotherms

Sorption of pesticides is generally evaluated by the use of sorption isotherms [18,20-22]. Batch equilibrium is a common technique used to determine soil sorption of pesticides. In a batch equilibrium technique, a series of solutions containing the pesticide to be tested at different concentrations are prepared. The solutions are then mixed with known amount soil and shaken until equilibrium is achieved. The concentration of the chemical in the solutions is then measured and a difference in the mass of the pesticide between at the start and at equilibrium is assumed to be due to adsorption by the soil particles. Then, the amount of pesticide adsorbed per unit weight of soil is calculated for each initial concentration of the pesticide. A relationship is then established between the pesticide concentration at equilibrium and the sorbed concentration of the pesticide by the soil [23].A sorption isotherm shows a relationship between the amount of pesticide adsorbed per unit weight of the soil and the pesticide concentration in the solution at equilibrium. The empirical classifications of sorption isotherms are divided into four main classes according to shape of the sorption isotherm. The S-type isotherms are common when the solid has a high affinity for the solvent. The initial direction of curvature in the S-type isotherm indicates that adsorption becomes easier as concentration increases. The L-type isotherm represents a relatively high affinity between the solid and solute in the initial stages of the isotherm. As more sites in the substrate are filled, it becomes increasingly difficult for the pesticide to find available sites for sorption to take place. The C-type isotherm is depicted by a pesticide that penetrates into the soil more readily than water molecules. The H-type isotherm is quite uncommon and occurs only when there is a very high affinity between a pesticide and the soil. The most frequently used isotherms for pesticides sorption are the Freundlich, Langmuir, and linear isotherms [24,25].

1.3.1. Freundlich equation

The empirically derived Freundlich equation has been used to describe the adsorption of pesticides by soil, organic matter and clay minerals [22]. The Freundlich equation can be expressed as:

$$\frac{X}{M} = K_f C^{1/n} \tag{1}$$

Where X/M is the ratio of pesticides to the adsorbent mass, C is the pesticides concentration in solution upon achieving equilibrium, and Kf (Freundlich coefficient) and 1/n are constants. In comparing adsorptive capacities of various pesticides by different surfaces, the Kf value may be considered to be a useful index for classifying the degree of adsorption. The necessary conditions are that 1/n values are approximately equal and experiments are conducted at the same C ranges. Cheah et al. (1997) [26] studied the adsorption, desorption of four commonly used pesticides in Malaysian agricultural soils. Their results indicated that adsorption of 2,4-D, lindane, paraquat and glyphosate to the sandy loam and muck soils followed a Freundlich adsorption isotherm. High adsorption values were obtained for paraquat and glyphosate in the soils. The adsorption values of 2, 4-D and lindane were much lower than paraquat and glyphosate. Adsorption values of pesticides in the muck soil were higher than sandy loam soil. Desorption of 2, 4-D and lindane was observed from the sandy loam soil and muck soil but paraquat was not desorbed. Glyphosate was not desorbed from muck soil but it was desorbed from sandy soil.

1.3.2. Langmuir sorption equation

The Langmuir adsorption equation was initially derived from the adsorption of gases by solids using the following assumptions: (i) the energy of adsorptions is constant and independent of surface charge; (ii) adsorption is on localized sites and there is no interaction between adsorbate molecules; and (iii) the maximum adsorption occurs as a complete monolayer. The Langmuir adsorption equation may be expressed in terms of concentration in this form:

$$\frac{X}{M} = \frac{(K_1 K_2\, C)}{(1 + K_1 C)} \tag{2}$$

The terms X/M and C have been defined earlier, K_1 is a constant for the system dependent on temperature and K_2 is the maximum adsorption capacity. The reciprocal of Langmuir adsorption equation is given by:

$$\frac{1}{\frac{X}{M}} = \frac{1}{K_2} + \frac{1}{(K_1 K_2\, C)} \tag{3}$$

A plot of 1 ⁄ (x⁄m) against 1⁄C, should give a straight line with an intercept of $1/K_2$ and a slope of $1/K_1K_2$ when the Langmuir relation holds. The adsorption of a number of pesticides on various soil surfaces was found to conform to an isotherm type which was similar to Langmuir model for adsorption. Under certain conditions both the Freundlich and Langmuir equation may be reduced to a linear relationship. In the case of the Freundlich equation, if the exponent 1⁄n is 1 the adsorption will be linearly proportional to the solution concentration. In practice, it has been generally found that sorption of pesticides on soil surface is according to the Freundlich equation with an exponent close to unity. In the case of the Langmuir, the denominator $1+K_1C$ becomes indistinguishable from 1 at low concentration. Thus, the amount adsorbed becomes directly proportional to the concentration in solution.

1.4. Factors affecting sorption of pesticides in soils

1.4.1. Characteristics of pesticides

Knowledge of pesticide structure and some physico-chemical properties often permits an estimation of its sorption behavior. Main characteristic of pesticides is that most of them are generally low molecular weight compounds with low solubility. The chemical characteristic, shape and configuration of the pesticides, its acidity or basicity, its solubility, the charge distribution on the molecule, the polarity of the molecule, its molecule size and polarizability all affect the sorption-desorption by soil colloids [8]. Four structural factors determine the chemical character of a pesticide molecule and influence its sorption on soil colloids. First, the nature of functional groups such as carboxyl, carbonyl, alcoholic hydroxyl and amino. The amino groups are especially important as they may protonate, depending on their pk and thus adsorb as cations. Both amino and carbonyl groups may participate in hydrogen bonding. In general, sorption is characteristically increased with functional groups such as R_3N^+, $-CONH_2$, $-OH$, $-NHCOR$, $-NH_2$, $-OCOR$, and $-NHR$ [8]. Secondly, the nature of substituting groups that may alter the behavior of functional groups. Thirdly, the position of substituting groups with respect to the functional groups that may enhance or hinder inter molecular bonding. Position of substituents may permit coordination with transition metal ions. Finally, the existence and size of unsaturated molecules which may influence the lyophilic-lyophobic balance [8]. The charge characteristic of pesticides is probably the most important property governing its adsorption [8]. The charge may be weak, arising from an unequal distribution of electrons producing polarity in the molecule, or it may be relatively strong, resulting from dissociation. The pH of a system is also an important factor as it governs the ionization of most of the organic molecules [27]. Acidic pesticides are proton donors, which at high pH become anions due to dissociation of hydrogen ion from the functional group [28]. The adsorption behavior of pesticides that ionizes in aqueous solutions to yield cations is different from those that yield anions. Furthermore, non-ionic or neutral pesticides behave differently from cationic, basic, or anionic herbicides. Neutral pesticides may be subjected to temporary polarization in the presence of an electrical field, which contributes to adsorption on charge surface. The availability of mobile electrons in the benzene ring, influence the polarization of a neutral molecule. Therefore, adsorption of neutral pesticide on charged surfaces may increase with molecular size when such increase involves the addition of an aromatic group [8]. Pesticide properties that affect mobility include aqueous solubility, hydrophobicity, ionizability, molecular size, volatility, and reactivity with soil constituents, and longevity in the environment [15].

1.4.2. Characteristics of soils

The soil solids are about 50% of the soil volume, the other half being filled by the soil water content and air. The major components in soils that have vital role to sorption of pesticides are clay, organic matter and dissolved organic matter (DOM) [29].

1.4.2.1. Soil clay minerals

The most important soil constituents for sorption of pesticides are clay minerals and organic matter [30,31]. Mineral soil colloids play an important role in sorption in sorption of polar, nonionic or ionizable pesticides [24]. They showed that an increase in clay content of soils significantly increased pesticide sorption. Nennemann et al. (2001) [32] showed that metolachlor was adsorbed by raw and purified bentonites but the amount adsorbed depends on the type of bentonite and pretreatment reactions. Modifying the bentonite or montmorilonite can enhance the adsorption. Pesticides containing polar functional group interact with clays through a variety of mechanisms [33]. These include interactions with exchangeable cations on clay surfaces via ion-dipole interactions, and with siloxane surfaces via surface adsorption. The ion-dipole mechanism may involve direct interactions of pesticides with exchangeable cations or indirect interactions through the intermediation of water molecules surrounding the cations. Ion-dipole interactions might be enhanced with increasing charge valence of the exchangeable cations. Clomazone and atrazine adsorption on montmorillonite saturated with a variety of cations decreased in the order of $Al^{3+} > Mg^{2+} \geq Ca^{2+} > Li^{+} > Na^{+}$ [34]. For the Al^{3+}- saturated clays, strong polarization of water molecules associated with Al^{3+} manifests strong H-bonding with pesticides induced greater adsorption [34]. Alternatively, the water molecules surrounding cations such as Ca^{2+} and Mg^{2+}can weaken ion-dipole interactions by inhibiting the direct interaction between polar functional groups and these cations [35]. Non-polar interactions between pesticides and the siloxane surfaces of clays may also occur [36]. In clays contain less strongly hydrated cations, the smaller the size of the hydrated cation results in an increase in size of adsorptive domains among the exchangeable cations, hence, enhancing pesticides sorption to siloxane surfaces. Jaynes and Boyd (1991) [37] determined the adsorption of aromatic hydrocarbons on trimethylphenyl ammonium-saturated smectites and found that adsorption increased as clay layer charge and exchanged organic cation content decreased, implying that the exposed clay siloxane surfaces are the effective adsorptive sites. Other researchers have noted that the adsorption of pesticides on clay siloxane surfaces increased with decreasing clay surface charge density and decreasing hydration energies of exchangeable cations [38].

1.4.2.2. Soil organic matter and dissolved organic matter effects on sorption of pesticides

Soil organic matter plays an important role in affecting the sorption of pesticides in the soil environment [39]. It contains compounds that can be conveniently be grouped into non-humic and humic substances. Non-humic substances include those with definite chemical characteristics such as carbohyrdrates, proteins, amino acids, fats, waxes and low molecular weight organic acids. Most of these substances are relatively easily attacked by microorganisms and have a comparatively short life span in soil. Humic substance by contrast, is more stable and constitutes the bulk of the organic matter in most soils. Humic substances are known to be rich in stable free radicals, which most likely play important roles in polymerization and depolymerization reaction and in reaction with other organic molecules, including pesticides and toxic pollutants. Soil organic matter may serve conflicting roles in mitigation of pesticide transport through soil. The fact that increasing soil organic matter increases the value of K_d has been reported in numerous publications and is a well-recognized phenomenon [40]. Organic matter is reported as a main component controlling sorption of many pesticides in soils [41]. It is known from previous studies that sorption of non-ionic pesticides by soil in aqueous system is controlled mainly by the organic matter content of the soils [42]. Sorption of pesticides has been reported to increase by amending soils with organic matter [25,43]. Soil organic matter can be divided into water dissolved and solid fraction and both can associate with pesticides. Dissolved organic matter (DOM) may affect the pesticide sorption and may increase the pesticide movement [44]. Ben-Hur et al. (2003) [45] studied the effects of the DOM on soil affinity for atrazine. Their results indicated that soil with high organic matter had higher affinity for atrazine. They also observed that DOM decreased atrazine sorption by soil but it was only apparent in soil with low organic matter content. Sorption capacities of soils for three pesticides (2, 4-D, naphthalene and chlorpyrifos) were shown to be significantly reduced with increasing DOM concentration in solution [46]. Cox *et al*. (2007) [47] studied the effects of mixing DOM from liquid waste and solid residue of an olive-mill with soils on the sorption coefficients of diuron and they found that sorption of diuron increased in sandy soil, whereas in clay soil sorption was decreased. They argued that the DOMs used in their study were composed of very poorly humified molecules, and were strongly sorbed onto the soil clay fraction, thus competed with diuron for the same sorption site. However, in a study using poultry compost and urban sewage sludge, Dolaptsoglou *et al*. (2007) [25] reported that DOM extracted from these materials was not interacting with terbuthylazine. Soils amended with these materials had higher sorption capacity for terbuthylazine as compared to the non-amended soils. An increase in pesticide sorption in soil amended with organic matter has also been reported by Senesi *et al*. (2001) [48] who found higher sorption of alachlor, imazethapyr, and rimsulfuron in soil amended with sewage sludge and they suggested multiple binding mechanisms responsible for the sorption which includes hydrogen bonds, ionic bonds and charge-transfer bonds. Several researches have reported the association of napropamide with DOM derived from sewage sludge amended soils [22,49]. They revealed that a napropamide and DOM complex was irreversible. Lee and Farmer (1989) [50] showed that napropamide can associate with humic and fulvic acids, but the affinity of dissolved humic acid for napropamide was higher than the dissolved fulvic acid. Their results also suggested that the source of the DOM should be taken into account when evaluating the interaction between DOM and napropamide. Lee *et al*. (1990) [51] studied competition between DOM and napropamide for sorption sites on clay and they found that DOM reduced the sorption of napropamide onto the clay and the extent of competition depended on the source and concentration of DOM. However, Sadegh-Zadeh *et al*. (2011) [18] reported that DOM derived from chicken dung (CD) and palm oil mill effluent (POME) did not interact with napropamide applied to sandy soils. Also, DOM did not decrease soil sorption capacity for napropamide. Studies on the effects of DOM on pesticide sorption by soils have produced contrasting results. This may be due to several factors including heterogeneity of soil properties, pesticides characteristics, and the different characteristics of DOM, based upon the sources they are derived from [52]. Conflicting results were reported in the literature on the effects of soil organic matter (SOM) on napropamide sorption in the soils. Aguer*et al*. (2000) [24] indicated that sorption of napropamide onto bulk soil was affected only by clay content but not the organic matter content. In contrast, other studies reported strong correlation between soil sorption of napropamide with SOM content but only slight correlation with clay content [1,4] Sadegh-Zadeh *et al*. (2011) [18] reported that the K_f value for napropamide sorption by the non-amended sandy soil (0.22) was lower than the value of 2.88 reported by Aguer*et al*. (2000) [24] for a soil containing 90% sand and 3% clay. The sandy soil used in study of Sadegh-Zadeh *et al*. (2011) [18] contained more than 99% sand but no clay was present. The organic matter of Aguer *et al.* (2000) [24] soil sample was 0.5% as compared to total organic carbon (TOC) in the Sadegh-Zadeh *et al*. (2011) [18] soil of 0.32%. Since the amounts of organic matter in both samples were low, the presence of clay in Aguer *et al*. (2000) [24] soil sample might be the reason for the higher sorption of napropamide in their study. The K_f values for sandy soil amended with 80 Mg ha^{-1} POME and CD were 2.05 and 6.62, respectively [18]. Both the amended soils had TOC of 1.2%. With a comparable amount of TOC, the K_f value for POME amended soil was approximately similar to the value of 2.94 reported by Gerstl and Yaron (1983a) [1] (1.18% OC) but the K_f value for CD amended soil was higher than amount reported by Gerstl and Yaron (1983a) [1]. Other studies have also reported significant increase in napropamide sorption with increasing soil organic matter [53]. The sorption mechanisms of nonionic compound like napropamide by organic matter are often very complex, involving hydrophobic interaction [42], and in some cases hydrogen bonding and electron donor-acceptor processes [54]. The result of Sadegh-Zadeh *et al*., (2011) [18] suggests that sandy soil has almost negligible potential to adsorb napropamide, the pre-emergence herbicide. Since napropamide is directly applied to the soil, it can freely move in this soil and therefore its downward mobility will also be very high. Therefore, amending this soil with organic matter especially the CD can be useful to enhance the soil sorption capacity for napropamide [18]. Sadegh-Zadeh *et al*. (2012b) [55] reported that the decreasing K_f values for selected Malaysian soil series were in the following order: Linau > Teringkap > Gunung Berinchang > Jambu > Rudua > Baging soil. Their results indicated that sorption increased with increasing clay and OC contents of the soils. Linau had the highest amount of clay and OC content, hence, it has the highest amount of sorption capacity to adsorb napropamide. Among the soils, the Baging series has the lowest sorption affinity for napropamide as it also has to the lowest amount of clay and OM content. Other researchers have reported that the napropamide sorption in arid and temperate soils depends on soil OM and clay content [1,24]. Soils that have higher napropamide sorption capacities are able to keep napropamide longer in the soils and reduced its mobility. Therefore, the contamination of ground water, surface water and finally the environmental contamination from napropamide will also be restricted in these soils.

1.4.3. Effects of biochars application on pesticides sorption in soil

Biochars are able to affect the fate of pesticides in the soil environment [56- 58]. Gámiz et al. (2017) [59] investigated the effect of biochars on the efficiency of herbicides include clomazone (CMZ) and bispyribac sodium (BYP). They evaluated the sorption, persistence, and leaching of clomazone (CMZ) and bispyribac sodium in biochar incorporated soil. Sorption of CMZ and BYP was higher in soil amended with biochar produced at 700 °C. However, the sorption of the CMZ was grater in soil amended biochar produced at low temperature. The Dissipation of CMZ increased after addition of biochars to soil. The persistence of BYP was up to 3 times greater when biochars 700 °C was invorporated to the soil. All biochars decresed the leaching of CMZ and BYP. Incorporation of biochar which produced at 700 °C deminished the action of CMZ against weeds, however, biochars produced at low temperature did not decrease the action of herbicides against weeds. The action of preemergence herbicides against weeds depend on biochars sorption and chemicals properties. Cabrera et al., (2014) [60] determined the effect of various biochars on the sorption of the herbicides aminocyclopyrachlor and bentazone and the fungicide pyraclostrobin on silt loam soil. Their results showed that aminocyclopyrachlor and bentazone were almost completely sorbed by the soils amended with the biochars produced from wood pellets. However, lower sorption of the herbicides was observed in the soils amended with the biochar produced from macadamia nut shells compared to non-amended soil, which was due to the competition between DOC derived from the biochar and the herbicides for sorption sites. The pyraclostrobin was highly sorbed to soil, and the addition of biochars to soil did not further increase its sorption. Therefore, they concluded that addition of biochars to increase the retention of low mobility pesticides in soil was not necessary, wile, biochars with high surface areas and low DOC contents could increase the sorption of highly mobile pesticides in soil.

1.5. Degradation of pesticides

Degradation of pesticides is an important process that determines the fate of pesticides in soil and water environments [1,61]. Degradation of pesticides in soil has been studied using several methods, such as extraction and chemical analysis, bioassays, oxygen uptake, and evolution of carbon dioxide. Some of these methods have been used in studies comparing sterile versus non-sterile soils. In general, conditions that promote microbial activity enhance the rate of loss, and those that inhibit the growth of microorganisms reduce the rate. Walker *et al*. (1993) [62] reported the half-lives of napropamide to be 60, 21 and 8 days in soil treated with the napropamide for the first, second and third time, respectively. They found that mixed bacterial cultures were able to degrade napropamide as proved by the inefficiency of an antifungal chemical (cycloheximide) to inhibit napropamide degradation as compared to an antibacterial chemical (chloramphenicol). In another study, they found that the half-lives of napropamide at first application were 25, 45 and 75 days in soils incubated at 25, 15 and 5 °C, respectively [63]. Application of small amount of previously treated soil to previously untreated soil introduced rapid degradation of napropamide [63]. Sadegh-Zadeh *et al*. (2012a) [64] reported that the data on napropamide degradation in Malaysian selected soils fit well to the first-order kinetics and the shortest and longest half-lives among soils were observed in Baging and Linau soil series, respectively. The decreasing half-life values were in the following order: Linau > Teringkap > Gunung Berinchang >Jambu > Rudua > Baging soil. The results indicated that degradation decreased with the increasing K_f of the soils. There was significant correlation between soil sorption of napropamide, as represented by K_f, and the half-life of napropamide in either sterilized or non-sterilized soils. Linau has the highest K_f, hence, napropamide half-life in this soil was also the highest. Among the soils, the Baging series has the lowest half-life as it also has the lowest sorption affinity for napropamide. Ng *et al*. (1995) [65] identified soil organic carbon, water table depth, soil moisture content, soil structures, antecedent days and time after application as the leading factors influencing the dissipation of atrazine and metolachlor. Their results illustrate that pesticides loss is independent of spatial variation. The degradation rates of pesticide for the aqueous phase were 2 to 4 times greater than the degradation rate in soils, depending on the soil type and the organic carbon fraction. Degradation of atrazine in soil has been shown to depend on soil pH; when soil pH increased, degradation of atrazine decreased [66].

Atrazine degradation was reduced in the presence of high inorganic nitrogen levels [67,68].

1.5.1. Kinetics of pesticides degradation in soil

Knowledge of the pesticides degradation kinetics is essential to the evaluation of them in soils. Once degradation of pesticide initiates, the amount disappeared with time and the shape of the disappearance curve will be a function of the pesticide concentration, the microorganisms responsible, and a variety of environmental factors. Information on degradation kinetics is vital since it characterizes the concentration of the pesticide remaining at a particular time, permits assessment of whether the pesticide will be eliminated before it is transported to a site which susceptible humans, animals or plants may be exposed. Such knowledge is thus essential for the assessment of the potential risk of harm associated with the exposure of susceptible individuals and species to the pesticides. Several models have been proposed to represent the kinetics of degradation in soils. These include Michaelis-Menten, zero-order, half-order, first order, second order and mixed-order models [69,70]. An understanding of when to use these models and why they may fail to describe the data requires knowledge of theoretical bases for these models. The models commonly used to fit data from evaluation of degradation in soil are, in essence, either empirical or theoretical. An example of empirical approach is the power rate model [6].

$$-\frac{dC}{dt} = kC^n \tag{4}$$

where C is pesticide concentration, t is the time, k is the rate constant for pesticide disappearance, and n is the fitting parameter. This model can fit to pesticide-disappearance curves by varying n and k until good fit is achieved. From this equation, it is evident that the rate is proportional to a power of the pesticide concentration. When n = 1, the model is equivalent to the first-order kinetics, and it is often has been used in this form [6]. When n = 0, the model reduces to zero-order kinetics, and when n = 2, it is presented by the second order kinetics. A plot of the logarithm of the pesticide concentration remaining against time gives either a straight, concave down, or concave up for first-, zero-, or second orders of reaction, respectively [6]. Pesticide half-life is calculated using the following equation:

$$t_{1/2} = \frac{\ln 2}{k} \tag{5}$$

where$t_{1/2}$ is the pesticide half-life.

1.5.2. Biodegradation of pesticides in soils

Microbial degradation plays an important role in the fate and behavior of the pesticides in soils [71]. Factors affecting the microbial degradation of pesticides in soil include pH, temperature, sorption, soil water content and soil type. Degradation of three herbicides widely used on agricultural crops, diuron, chlortoluron and bromacil, were assessed in laboratory studies by monitoring $^{14}CO_2$ production from treated soils [72]. The degradation was slow with no indication of a lag phase. Diuron and chlortoluron breakdown was higher in the loamy sand soil than in organic soil, whereas bromacil degradation was essentially unaffected by soil type. The effect of temperature on the degradation process was more pronounced than the effect of soil type. Soil microorganisms are able to interact physically and chemically with pesticides and inducing the physical change or the complete change of pesticides [73,74]. Soil microorganisms metabolize pesticides either aerobically or anaerobically and usually microorganisms degrade the pesticides and utilize them as a source of energy and nutrients [75] or use them through co-metabolism [76].

1.5.3. Pesticides degradation in organic maters amended soils

Chantigny (2003) [77] indicated that incorporation of organic matter to soil could increase the concentration of DOM. The addition of organic amendment to soil normally results in an increase in the microbiological activity due to the availability of simple organic molecules such as sugar and amino acids to the microbes [78]. Many studies have been conducted to determine the influence of organic matter added to soils on degradation of pesticides [53,79,80]. Dolaptsoglou *et al*. (2007) [25] reported that the addition of urban sewage sludge, corn straw and poultry compost in agricultural soil reduced the degradation rate of terbuthylazine. On the other hand, other studies have demonstrated that organic matter amendment has no effect on pesticide degradation. Getenga and Kengara (2004) [81] reported that there was no effect of compost amendment on degradation of glyphosate in soils. However, in his earlier study Getenga (2003) [82] found that compost added to the same soil increased atrazine degradation. The incorporation of organic amendments to soil may decrease mineralization of pesticides by increasing pesticide sorption [48]. However, amendments can also accelerate or enhance biodegradation by stimulating microbial growth due to nutrient incorporation to the soils [67,76,78]. Sadegh-Zadeh *et al*. (2012a) [64] reported that degradation of napropamide in non-amended and amended sandy soil with CD and POME fit the first-order kinetic well. The half-life of napropamide was longest in the soil amended with 20 Mg/ha CD and the shortest half-life was observed in the non-amended soil. Napropamide degradation was retarded in soils amended with either CD and POME and this was due to sorption of napropamide by both organic amendments, which protect the chemical from being biodegraded. Other researchers also showed that incorporation of organic materials into soils could reduce degradation of pesticides [48,53,83,84]. In the sterilized treatments, the half-lives of napropamide were similar to the non-sterilized treatments with the shortest half-life (69 d) observed in the non-amended sandy soil and the longest half-life was in the CD-amended sandy soil [64]. However, half-lives of napropamide in the sterilized treatments were significantly higher than in the non-sterilized treatments which indicated that microorganisms were responsible for the napropamide degradation. Other studies have also indicated that biodegradation was a key factor in the napropamide degradation [62,63]. In the non-sterilized soils, removal of DOC reduced the half-life of napropamide [64]. Degradation of napropamide was retarded by DOC application as indicated by the longer half-lives with increasing rates of DOC [64]. In the sterilized treatments, however, there was no effect of DOC on the napropamide degradation. Breugelmans *et al*. (2008) [85] showed that the presence of a more easily degradable DOC as additional carbon sources inhibited 3, 4-DCA biodegradation. In another study, they determined whether the linuron degrading performance of a multi-species bacterial biofilm is affected by co-occurrence of multiple nutrient sources and they found that the addition of alternative carbon sources at different concentrations resulted in diminished linuron degradation efficiency [86]. The bacterial community may be is responsible for napropamide biodegradation in soils [62]. However, Sadegh-Zadeh (2010) [87] showed that napropamide degradation was lower in the amended Baging soil whereas bacterial population was highest in this soil. This suggests that napropamide degradation was controlled by soil sorption capacity rather than the soil bacterial population [87]. This result is not consistent with the result of Cox *et al*. (2001) [78] reported that that organic matter addition to soil increased pesticides biodegradation. The conflicting reports on biodegradation of pesticides in soils suggest that biodegradation depends on many factors including:

1) Diffusion barriers that may limit or prevent contact between microbial cells and pesticides.
2) Biodegradation of sorbed pesticides on clays or humus constituents may be quite different from the pesticides that are free in solution.
3) The presence of other organic molecules that can be metabolized by the biodegrading species may decrease or enhance use of the pesticides.
4) The supply of inorganic nutrient may govern the rate of pesticides degradation by microbes.
5) Protozoa or possibly species parasitizing the biodegrading populations may govern the size, or activity of the populations responsible for the biodegradation.
6) Many pesticides have exceedingly low solubility in water and they have low biodegradation rate while other molecules with high solubility are more available to the soil microbes [84]. Tang et al. (2017) [88] applied Fe-impregnated Biochar to sorb Chlorpyrifos, reduce uptake by *Allium fistulosum* L. and enhance Microbial Community diversity. Fe-impregnated biochar showed a higher sorption capacity than pristine biochar and removal higher chlorpyrifos from the water. Their results indicated that the Fe-biochar was more effective in reducing uptake of chlorpyrifos by plant. The Fe-biochar altered microbial communities. The study of Zhang et al. (2016) [89] revealed that biochar incorporation to the soil enhanced soil sorption of diethyl phthalate, however, increasing the adsorption capacity was dependent on the soil organic carbon amount, and aging of biochar.

1.5.4. Chemical and photo-decomposition of pesticides

Chemical conversion and degradation of pesticides in soils are widespread phenomena that plays important role in the dissipation of pesticides in the soil environment. Chemical degradation of pesticide by hydrolysis and oxidation is a common process. Nucleophilic substitution reactions, other than hydrolysis, may take place with reacting groups of soil organic matter. Reaction between pesticides with free radicals in soil is also a possibility. Chemical degradation of pesticide that occurs in soil may be catalyzed in several different ways and they occur by clay surface, metal oxides, metal ions and organic matter. Solar radiation is responsible for many chemical changes of pesticides in the environment. Within the range of ultraviolet (UV) sunlight wavelengths, sufficient energy exists to bring about many chemical transformations of pesticides. Often the degradation products are identical with those produced by chemical and biological reactions; however, photodecomposition has produced some unique structures. For photodecomposition to take place, the sunlight must come in contact with the pesticides. Since penetration of UV light into solid matter is limited, photodecomposition of pesticides in soil is restricted to residues close to the surface. The extent of photodecomposition depends on the duration of exposure, the intensity and wavelengths of light, the state of the chemicals, and the presence of water and air. Photodecomposition of chemicals has been reported for a wide range of pesticides used in agriculture. However, the role of photochemical reactions in the degradation of pesticides in soil is uncertain, as most of these reactions have been reported under conditions involving exposure to high intensity light and frequently in non-aqueous solvents. Photodecomposition may be of considerable importance for pesticides applied to the soil surface. Photolysis is an important factor in the degradation of napropamide. Donaldson and Miller (1996) [90] showed that if napropamide can move to the soil surface by evaporation, then it can be degraded by sunlight irradiation. Photolysis of pesticides in soil is effectively limited to the top 0.5 mm of depth surface. Consequently, processes that move napropamide to this sunlight-irradiated zone may have a significant impact on the degree of photolysis in soils. The effect of upward transport in translocation napropamide into the photic zone was examined using an experimental system in which soils were supplied with water at their base [90]. Photolysis rates were much greater than the predicted values if photolysis had been limited to the soil surface, with up to 70% lost in a 3 cm deep loamy sand soil after 14 days of irradiation as compared to dark control. Rates of loss were slower in sandy clay loam, with 29% loss over 14 days. Rates of transport were affected by sorption, with measured values of the distribution coefficient (K_d) of 0.4-0.72 and 6.6-7.2 mL/g in loamy sand and sandy clay loam soils, respectively. In soil with high potential upward movement of napropamide, photodegradation of napropamide was high. They demonstrated that in soil with relatively high sorption capacity, photodegradation was controlled by the movement of chemical to the irradiation zone; while in soil with low sorption capacity, photodegradation was controlled by the photoreactivity of the chemical.

1.6. Leaching of pesticides in soils

Knowledge of pesticides leaching is important to understand the problems of contamination of natural water and soil environments [52,61,91,92]. Pesticides mobility is governed by the interactions of specific physical and chemical properties of soils which determine the potential bonding mechanism and magnitude of retention to soil. Cheah *et al*. (1997) [26] studied the mobility of four commonly used pesticides in Malaysian agricultural soils. Their results showed that only 2, 4-D was mobile in the sandy loam and muck soils. Paraquat and glyphosate were not leached out from the soil profile, while leaching of lindane was observed in the sandy loam soil. Leaching of pesticides can be represented by the breakthrough curves (BTC). Analysis of the collected effluent from the soil matrix at one end of a disturbed or undisturbed soil column shows a change in the composition of effluent solution with respect to time or amount of effluent. The graphical representation of the concentration of the pesticide with respect to time or cumulative effluent volume or pore volume is known as a BTC. Leaching of pesticides through soil in the solution phase may involve diffusion and mass flow processes [93]. The important factor of diffusion processes in soil water is the pesticide solubility. Diffusion is the process by which matter is transported as a result of random molecular motion caused by their thermal energy. Therefore, there is a net movement from areas of higher concentrations to areas of lower concentrations. Mass flow occurs as a result of external forces acting on the carrier for the pesticide under discussion. Leaching of pesticide is usually considered synonymous with mass flow, although diffusion occurs simultaneously. The summation of diffusion and mass flow processes determines the total rate of movement of pesticide in soil. Under preferential flow condition, water and pesticide move only through a portion of the available pore space or at least markedly faster in certain soil parts than in others. Preferential flow can occur in well-structured clayey soil as well as in poorly structured sandy soils. Reichenberger *et al*. (2002) [94] found that measured pesticide displacement reached deeper soil layer than the predicted depth using a leaching model. They argued that the main reason for this phenomenon is the preferential flow of the pesticide. Leaching of pesticide in unsaturated soil is largely determined by the physical and chemical properties of both the pesticide and soil. However, rates of pesticide leaching that are faster than would have been expected from these properties have been reported in a number of studies [94]. This has often been attributed to the existence of preferential flow paths in the unsaturated zone, which provides faster transport than those predicted by the sorption-desorption processes [95]. Preferential flow is assumed to be largely responsible for chemical transport in the soil, particularly of pesticides that are moderately or strongly adsorbed onto soil components [96]. Pesticides are leached by this mean during the few weeks after treatment, when they are available on the soil surface. Rapid flows occur in large, vertical and continuous channels in the soil. In field conditions, the preferential flow event is transient and it can be assumed that lateral dispersion along walls causes water flow in large pores to slow down and to progressively occur in finer pores as matrix flow [97,98]. Therefore, pesticides transport through the vadose zone is governed by soil properties including organic matter content and the thermodynamic properties of the pesticides such as water solubility and volatility. Movement of organic chemicals through soil is usually retarded by the presence of adsorptive soil constituents. Soil organic matter provides most of these sites for organic sorption in natural soils [99]. Gerstl *et al*. (1981) [100] reported that the application of napropamide to previously wetted soils increased the vertical and lateral movement of napropamide. However, napropamide distribution in the initially dry soil showed a very sharp concentration gradient. In other study, Gerstl and Albasel (1984) [101] investigated the effects of irrigation frequency on the mobility of napropamide in soil irrigated with a drip irrigation system and they found that napropamide was only slightly mobile and the increase in water application rate resulted in greater lateral movement of napropamide. Ghodrati and Jury (1992) [102] investigated the effects of soil structure, different formulation of three pesticides (atrazine, napropamide and prometryn) and irrigation methods on preferential flow of these pesticides in unsaturated soil. They found that most of the pesticides were retained in the top 10-20 cm, but there were considerable movement below this zone. There was occurrence of extreme mobility or preferential flow of pesticides under every experimental condition except when pesticides were applied in wettable powder from pots containing soils that were surface-tilled and repacked. This finding implies that there may be fine preferential flow pathways through which solution may move but particulates may not. The pesticides application, stringent authorization procedures, market instruction, and an introduction of thresholds pesticides concentration in groundwater need revision [103].

1.6.1. Leaching of pesticides in organic matter amended soils

Many studies have been conducted to determine the influence of organic matter amendments on pesticides movement in soils. [80]. Amendment of soils with organic matter may modify sorption and leaching of pesticides in soil. Some studies showed that organic matter added to soils reduced pesticides in ground water [67,78]. The advantage of pesticide sorption by organic amendments is the restriction of pesticides leaching in soils [2]. The incorporation of composted and raw organic matters increased the retention of pesticide in the soils [45]. Albarrán *et al*. (2004) assessed the behavior of simazine in soil amended with two rates of solid olive-mill waste and found that the amendment retarded the vertical movement of the pesticide through the soil and greatly reduced the amount of pesticide available for leaching. Sadegh-Zadeh *et al.* (2012a) [64] clearly showed that organic matter addition delayed the leaching of napropamide from a sandy soil column. García-Jaramillo *et al*. (2014) [104] reported the effects of organic residues from different olive oil production on the sorption and leaching of bentazone and tricyclazole. Their results showed a slight delay of bentazone in soil amended with olive oil production waste and biochar. Moreover, the amending of soil with both of olive oil production waste and biochar significantly decreased the leaching of tricyclazole from the soil. Varsha *et al.* (2015) [105] reported that application of cereal straw to soil decreased 22% of chlorpyrifos leaching.

1.6.2. Effect of dissolved organic matter on leaching of pesticides in soils

Other factor that has an important role in the movement of pesticides in soil profile is the formation of pesticides-dissolved organic matter complexes. Soil organic matter can be a source of dissolved organic matter. Dissolved organic matter is able to complex with the pesticides and increases the mobility of pesticides in the soil profile. Dissolved organic matter is able to affect the dissolution and facilitated the transport of pesticides. Therefore, application of certain types of organic fertilizer to some agricultural soils may not be advantageous as far as pesticide leaching is concern because it may enhance or facilitate pesticide leaching through the soil profile. Nelson et al. (2000a) [22] showed that when napropamide complexes with dissolved organic matter, its mobility in soil was increased. In their study, a silt loam soil was used with and without sewage sludge amendment to represent differences in organic matter content. Results showed that less than 6% of the applied napropamide moved as dissolved organic matter complexes through soil while the majority of the complexed napropamide was very stable and relatively non-adsorbing in solution such that doubling of soil depth only reduced the facilitated transport by 20% or less [22]. This result showed that DOM can facilitate napropamide movement through soil and that sewage sludge-derived DOM may lead to enhanced napropamide transport in sewage sludge amended soil. Similar findings were reported by Williams et al. (2002) [99].

2. Conclusions

It is known from the studies that sorption of non-ionic pesticides by soil in aqueous system is controlled mainly by the organic matter content of the soils. Sorption of pesticides has been reported to increase by amending soils with organic matter. In general, conditions that promote microbial activity enhance the rate of pesticides degradation, and those that inhibit the growth of microorganisms reduce the rate of degradation. Amendment of soils with organic matter may modify leaching of pesticides in soil. Some studies showed that organic matter added to soils reduced pesticides in ground water. Overally, organic amendments induces the restriction of pesticides leaching in soils.

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