

Interaction of selected pesticides with mineral and organic soil components

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Abstract: The pesticide persistence, in particular in soils, often significantly exceeding the declarations of their manufacturers is surprising. There are many publications devoted to the explanation of this phenomenon in the field literature, but the diverse research methodologies used may lead to the ambiguous conclusions. On the basis of the collected literature, the attempt was made to systematize the available information on the interactions of commonly used groups of pesticides with individual soil components. The complex mechanisms of interactions between pesticides and soil based on van der Waals forces, ionic and covalent bonding, ligand exchange and charge transfer complexes formation were demonstrated. It was also proved that the nature of interactions is strictly dependent on the structure of the pesticide molecule. The conclusion of the review may contribute to the choice of plant protection products that, in addition to their effectiveness, are as little ballast for the environment as possible.

Introduction

Soil is a non-renewable resource essential for the vitality of ecosystems and, therefore, of mankind. Widely used plant protection products accumulate in soil leading to negative changes in biological properties of soil. The physical and chemical properties of soil also play a key role in the stability of pesticides in the soil environment (Romdhane et al. 2019, Rodríguez-Valdecantos et al. 2017). The degradation of pesticides in soil is a process regulated by both abiotic and biotic factors, which are influenced by a wide range of microbial interactions with soil components. Under EU directives, some of them (for example, atrazine, phorate) have been withdrawn from use in the EU countries. However, they can be used in other regions of the world. Furthermore, these compounds are found in soils (historical pollution) in the form of point and nonpoint sources pollution.

Due to low water solubility and moderate to high water hydrophobicity of many plant protection agents they are strongly adsorbed to soil particles (Pinheiro et al. 2015). The main factors influencing the persistence and mobility of pesticides in soil are adsorption and desorption. These processes affect the bioavailability of pesticides and thus play a key role in the sequestration of pollutants. Knowledge of these two processes is essential to assess the environmental risk of usage of agricultural chemicals, to conduct remediation of pesticide contamination and to develop pesticide disposal technologies. However, the information concerning this issue is dispersed and the conclusion is difficult to draw. Therefore, the aim of the review is to systematize the available information on the

interactions of selected groups of pesticides with individual soil components. The conclusions may contribute to the choice of plant protection products that, in addition to their effectiveness, are as little ballast for the environment as possible.

Characteristic of soil fraction

Depending on the ratio: organic matter – mineral fraction, the following types of soil may be distinguished: mineral soils, mineral-organic soils and organic soils. Bonding of pesticides in soil is determined by its qualitative (minerals including clay minerals, iron (hydr)oxides, quartz, etc. and natural organic matter (NOM)) and quantitative composition.

Organic components

Soils vary in adsorption capacity and mechanisms of pesticides binding due to the differences in their composition and diversity of their physicochemical properties. Soil organic matter (SOM), which consists of dead and living organic components, mainly of plant origin, is crucial for adsorption processes. Humic substances (HS) including fulvic acids, humic acids (HAs) and humin, with varying molecular weight and properties can be found in SOM. They are involved in soil structure, porosity, water capacity, cation and anion exchange capacity, and are involved in the chelation of mineral elements. The main functional groups of HS are: -OH, -OH, -COO⁻, -C=O (Cybulak et al. 2019). The ionization degree of HS depends on the amount of phenolic and carboxylic functional groups. HS are responsible for the transport and degradation of different types of xenobiotics. The uptake of different

pesticides by various organic matter fractions depends on their chemical composition, functionality and structure, including hydrogen bonding, ionic, charge-transfer processes, electrostatic (columbic) attraction and hydrophobic bonding. Moreover, HAs can bind clay minerals to form stable organic clay complexes.

Positive correlation between soil organic carbon content and adsorption of most pesticides results in a higher pesticide uptake in surface soil (Alletto et al. 2010). The adsorption properties of HAs are influenced by the presence of electron donating groups, which have the ability to interact with metal ions, and the presence of the bridges bonding acid aromatic rings, that are responsible for their porous structure (Donisa et al. 2003). The affinity of pesticides to different fractions of organic matter in soil affects their behavior in soil-aquatic ecosystems (Sun et al. 2012).

Inorganic soil components

Clay minerals, mainly kaolinite and smectite, as well as iron (hydr)oxides dominate the inorganic fraction of soil and control pesticide adsorption. In smectites there are isomorphous substitutions in tetrahedron and octahedron plates. These substitutions generate a constant negative charge, which is balanced out by the adsorption of cations on surface; the amount of these adsorbed cations corresponds to the clay cation exchange capacity (CEC) (Azarkan et al. 2016, Sidhoum et al. 2013). Apart from this permanent charge, the groups =SiOH and =Al₂OH, present in clay minerals, may be protonated or deprotonated.

The potential kaolinite adsorption sites comprise of hydroxyl groups on the mineral edges (silanol (=SiOH) and aluminol (=Al₂OH)) Another natural component of soils are iron compounds and other metals sesquioxides. Iron in soil occurs in the form of oxides and (hydr)oxides. They can form a free fraction as well as bind to clay minerals surface and HS, therefore modifying their surface properties and reactivity (Liu et al. 2013). Iron oxide minerals are characterized by high surface areas (up to 700 m²/g for ferrihydrite) (Cornell and Schwertmann, 2003) and high values of point of zero charge (pHZPC) in the 6.7–9.2 pH range and may bind cations and anions (Schwertmann and Cornell, 2000).

Types of interactions between pesticides and soil components

In contact with the soil environment, pesticides may: (i) be adsorbed by different soil components, (ii) transform to other compounds, sometimes even more dangerous than the original ones, (iii) leach from soil and pollute the surface or ground waters.

The adsorption equations are employed to describe the affinity between pesticides and adsorption centers of soils as well as adsorption mechanism. Moreover, the values of the parameters in the equations allow to estimate the binding energy and the maximum adsorption capacity. The most common models of adsorption are (Rani and Juwarkar, 2010; Seki and Yurdakoç, 2005):

– Freundlich isotherm – commonly used to describe the adsorption characteristics for an heterogeneous surface (Freundlich 1906),

$$q = K_F C_{eq}^{1/n} \quad (1)$$

– Langmuir isotherm – valid for the monolayer adsorption on a surface containing a finite number of identical sites

$$q = \frac{q_L K_L C_{eq}}{1 + K_L C_{eq}} \quad (2)$$

where:

q – amount of pesticides adsorbed on soil (mg/g),

C_{eq} – equilibrium concentrations of pesticides in the solution (mg/L),

K_F – Freundlich isotherm constant ((mg^(1-1/n)L^{1/n})/g),

$1/n$ – a function of the strength of adsorption in the adsorption process,

q_L – maximum monolayer coverage capacity (mg/g),

K_L – Langmuir isotherm constant related to the affinity of binding sites (L/mg).

The Langmuir model assumes uniform energies of the adsorption on the surface and no transmigration of the adsorbate in the surface plane (Langmuir 1916),

Adsorption has been identified as the primary process responsible for binding pesticides in soil. The adsorption process controls transport, bioavailability, release and degradation of organic pesticides in soil. In the literature, different models are used to describe the theory and models of adsorption, but most often the isotherms of Freundlich or/and Langmuir are used. Sadegh-Zadeh et al. (2017) showed that soil physical and chemical properties affect binding capacity, retention and mobility of pesticides in soil. The adsorption effects of pesticides on soil may occur on active centers of minerals or organic components or both and may be completely reversible or irreversible. The efficiency of adsorption processes can vary widely from total process irreversibility to full reversibility.

Pesticide residues can be adsorbed on soil components depending on different mechanisms and bonds. The schematic diagram of these processes is presented in Fig. 1.

In the case of van der Waals forces, hydrogen bond, hydrophobic bond, a purely physical adsorption takes place. However, for electrostatic interactions such as charge transfer, ion exchange or ligand exchange, chemical adsorption can occur. It should be noted that not all mechanisms are present at the same time. Increased persistence of pesticides in soil may result from chemical reactions between pesticides and/or their metabolites leading to the formation of stable compounds.

In diluted systems, competitive adsorption, which occurs at the water-solid interface with a limited number of active centers, is the result of surface adsorption. Pateiro-Moure et al. (2010) suggest that competitive adsorption plays an important role in the transport of soil contamination due to the diversity of organic compounds in the soil – water environment.

Hysteresis loop includes both adsorption and desorption processes. Numerous authors indicate that the hysteresis loop is the result of (i) irreversible binding or sequestration of the solute with organic carbon and/or clay mineral present in the soil (binding hysteresis) (Bhandari et al. 1996), (ii) retention of adsorbent molecules in micro and mesoporous mineral structures or organic carbon present in soil (structural hysteresis) (Carroll et al. 1994, Farrell and Reinhard 1994, Weber et al.

1998). In the case of desorption of pesticides from soils, both types of hysteresis occur, but it is difficult to determine which factor is prevalent. The structural hysteresis of a pesticide varies according to the meso- and micropore structure of the adsorbents. A higher hysteresis was found for desorption of pesticides from clay and silt fractions than from raw silt, which can be explained by higher organic carbon associated with the fractions and their higher structural hysteresis.

One of the processes affecting the transport of contaminants in soils is diffusion. Diffusion causes impurities to spread both in the soil solution and inside the organic matter structures.

Several types of diffusion are defined for pesticide molecules in soils: (i) diffusion within organic matter structures, (ii) diffusion within layers with different structures, and (iii) diffusion within mineral particles and in pores. The presence of a large number of pores with the smallest diameter (nanopores) causes a significant limitation of diffusion processes and an increase in the stability of contaminants (Pignatello 2000). Roy et al. (2000) have shown that the adsorption of pesticides in soils is influenced by both the physicochemical properties of the pesticide and the soil moisture. For soils with low moisture content, the humus substance is modified, resulting in more

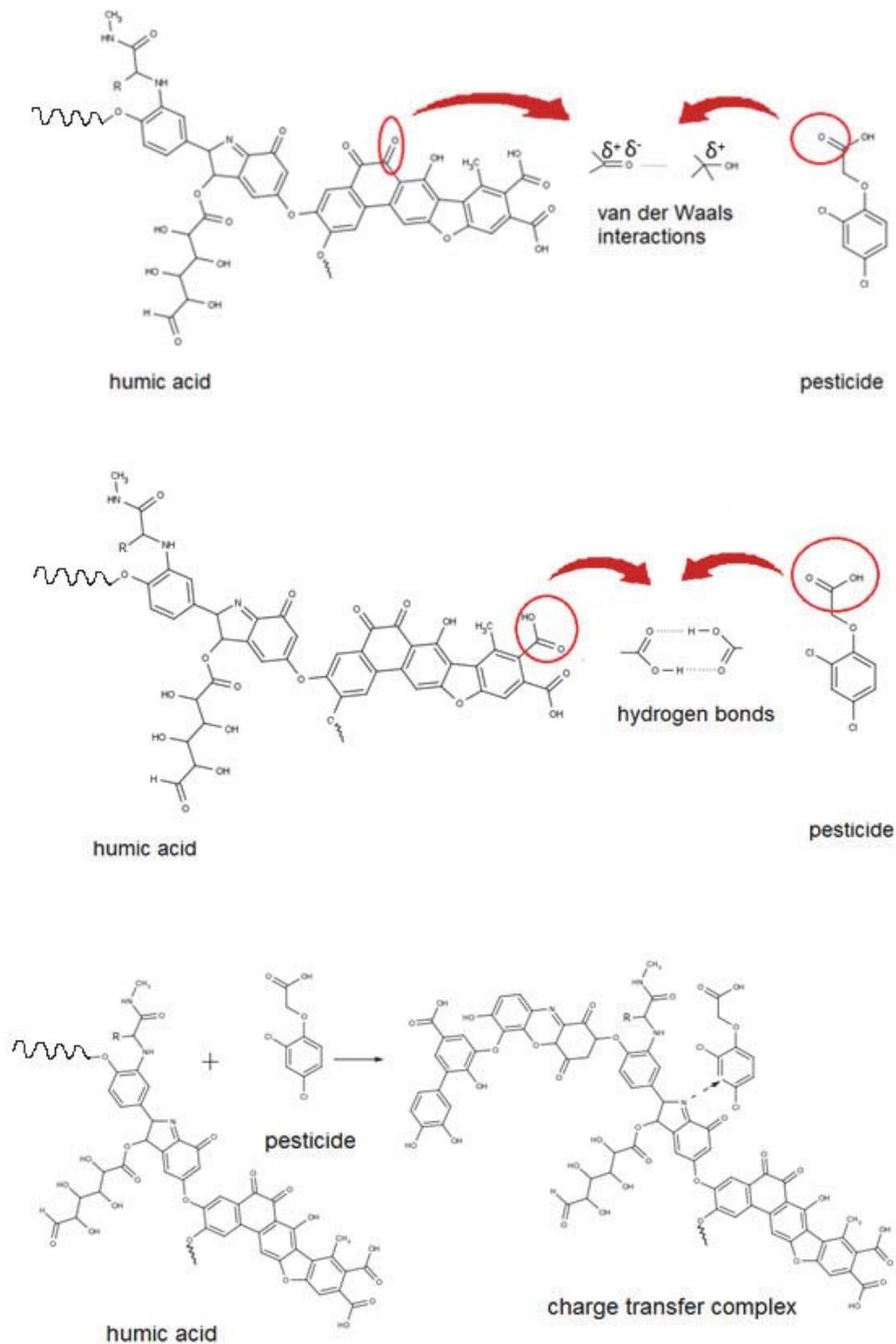


Fig. 1. Schematic diagrams of interactions of HAs with pesticides

hydrophobic surfaces favoring the adsorption of pesticides. On the other hand, high soil moisture, due to the affinity of hydrophilic compounds to hydrophilic humus regions, makes them more strongly sorbed. Taking into account the fact that pesticides disperse in water in the aggregates, it can be expected that mass transport of these compounds will be faster in moist soils.

Van der Waals interactions

Van der Waals forces are the interactions between a permanent and an induced (excited) dipole. This interaction is relatively weak in the case of small particles but can even exceed the chemical bond forces in the case of large particles. They occur in all adsorbent/adsorbate interactions. Their role is very important in the interaction of non-ionic and ionic pesticides with the molecules of HAs. Their importance increases with the size of the interacting molecule and its ability to adapt to the surface of the adsorbent (Senesi 1992). It is known that the van der Waals interactions decrease with the distance between molecules and therefore their role in the adsorption process is greater for pesticides in close proximity to the surface or able to maintain close contact with adjacent adsorbate ions.

Ionic bonding and H-bonds

Ionic bonds to soils can be formed between carboxylic and phenolic hydroxyl groups of humus substances and $-OH$ groups of clay minerals and iron oxyhydroxides. It should be noted, however, that due to the sterical effects it is not always possible to form this type of bonds (Senesi, 1993). Hydrogen bonds may be formed between humus substances and pesticides as a result of the presence of groups in their molecules capable of forming such interactions. Nevertheless, water molecules play an important role in competition for pesticides in the formation of hydrogen bonds. Numerous studies indicate that hydrogen bonding strongly influences the adsorption of some non-ionic polar pesticides. It has been proved that non-ionized forms of acidic and anionic pesticides, at pH conditions below their pKa, can form a hydrogen bond with soil organic matter with the participation of $-COOH$, $-COOR$ groups (Senesi 1993).

Covalent bonding

Rani and Juwarkar (2010) indicate that the formation of covalent bonds between some pesticides, including organophosphorus, and soil components is facilitated by a chemical or enzymatic catalyst. According to Liu and co-workers (2013), a mechanism of interaction between SOM and amorphous hydrated iron oxides (AHOs Fe) is possible. This phenomenon may result from the formation of a spherical complex due to columnar interaction and/or ligand exchange between $-COO^-$ SOM groups and hydroxyl groups on the surface of AHOs Fe. Due to their high degree of hydration, variable charge and large surface area of amorphous minerals, they can form stable mineral-organic bonds by exchanging ligands and anions.

Ligand exchange

Ligand exchange also occurs in adsorption processes and includes the replacement of weak ligands by pesticide molecules such as s-triazines and anionic pesticides (Nearpass 1976, Senesi 1992). This is favored by a change in entropy

when a xenobiotic molecule replaces water molecules bound with one or more complexed metal ions.

Charge transfer complexes

Humic substances are characterized by electron-deficient particles (e.g. quinones) and electron-rich centers (e.g. diphenols). The charge is transferred according to the electron-donor-acceptor mechanism, with the participation of pesticides that alternatively have the properties of an electron donor or acceptor. The mechanism of charge transfer between the humus substance and the pesticide can result in an increase in the concentration of free radicals. Charge transfer complexes also occur between electron acceptor centers in HAs and substituted fats and amitrole, which are capable of transferring electrons. Considering this process, Boyd et al. (2001) and Johnston et al. (2001) suggested a mechanism of complexation between the nitrate group of adsorbate and the exchangeable cation. Li et al. (2003, 2004) pointed out that the adsorption of nitroaromatic compounds can be dominated by strongly hydrated cations in clay materials, e.g. sodium or calcium ions. Other authors who attempted to explain the strong adsorption of nitroaromatic compounds by HAs of carbon origin suggested the possibility of π - π interaction (Zhang et al. 2005, Zhu and Pignatello 2005). Kodesová et al. (2011) indicated that the adsorption of pesticides on soil components depends mainly on the content of organic matter, pH, CEC and the saturation of the adsorption complex.

Pesticides behavior in soil

Knowledge of the chemical structure of pesticide and its physicochemical properties allows to predict its adsorption behavior. The type of functional groups of pesticides, especially $-CONH_2$, $-R_3N^+$, $-OH$, $-NHCOR$, $-NH_2$, $-OCOR$, and $-NHR$ together with charge characteristics seem to play a decisive role in adsorption processes (Sadegh-Zadeg et al. 2017, Tunega et al. 2010). For the review, the main groups of non-ionic pesticides and ionic pesticides (acidic pesticides, cationic pesticides, basic pesticides) were selected. They were chosen due to their extensive use and physicochemical parameters presented in Table 1. On the basis of collected information about these pesticides' behavior in soil, the stability of other compounds with similar structures may be concluded.

Non-ionic pesticides

Urea pesticides

Chlortoluron (CHL), diuron, linuron, and isoproturon (IPU), belong to the group of urea herbicides. Between urea herbicides and SOM strong hydrogen interactions and charge transfer are observed. CHL shows stronger interactions with SOM than IPU. This is due to the amide group in the CHL structure, which interacts more strongly with the carboxylic SOM groups. In contrast, electron-withdrawal properties of chlorine atom in the IPU structure do not promote the formation of hydrogen bonds with soil organic matter (Chefetz et al. 2004).

Adsorption of CHL on two different soils (organic carbon content was in the range of 1.1–5.6% and clay fraction was 25–30%) (Fouque-Brouard and Fournier 1996) indicated that the adsorption capacity of the soil with 5.6% of organic carbon for the CHL was lower than for chloroxuron and difenoxuron pesticides. Freundlich model very well simulates CHL

Table 1. Physicochemical properties of selected pesticides*

| Pesticide | Structure | logP | pK _a | Water solubility [mg/L] (20°C) | DT ₅₀ [day] | Remarks |
|---|-----------|-------|-----------------|--------------------------------|------------------------|----------------------------------|
| 2,4-D 2,4-dichlorophenoxyacetic acid | | -0.82 | 3.40 | 24300 | 4.4 | herbicide, acidic pesticide |
| Ametryn 2-ethylamino-4-isopropylamino-6-methylthio-1,3,5-triazine | | 2.6 | 10.1 | 200 | 37 | herbicide, basic pesticide |
| Atrazine 2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine | | 2.7 | 1.7 | 35 | 75 | herbicide, basic pesticide |
| Butachlor <i>N</i> -butoxymethyl-2-chloro-2',6-diethylacetanilide | | 4.5 | n.r. | 20 | 56 | herbicide, neutral pesticide |
| Chlorpyrifos O,O-diethylO-(3,5,5-trichloro-2-pyridyl) phosphorothioate | | 4.7 | no dissociation | 1 | 50 | insecticide, non-ionic pesticide |
| Chlortoluron 3-(3-chloro-4-methyl)-1,1-dimethylurea | | 2.5 | no dissociation | 74 | 45 | herbicide, non-ionic pesticide |
| Diquat 1,1-ethylene-2,2-bipyridyldiylum dibromide | | -4.6 | n.r. | 718000 | 2345 | herbicide, cationic pesticide |
| Isoproturon 3-(4-isopropylphenyl)-1,1-dimethylurea | | 2.50 | no dissociation | 70 | 12 | herbicide, non-ionic pesticide |
| Paraquat 1,1-dimethyl-4,4-bipyridinium dichloride | | -4.5 | no dissociation | 620000 | 3000 | herbicide, cationic pesticide |
| Phorate O,O-diethyl S-(ethylthiomethyl) phosphorodithioate | | 3.33 | n.r. | 50 | 63 | insecticide, non-ionic pesticide |
| Terbutylazine N-tert-butyl-6-chloro-N'-ethyl-1,3,5-triazine-2,4-diamine | | 3.4 | 1.9 | 6.6 | 75 | herbicide, basic pesticide |
| Terbutryn N2-tert-butyl-6-chloro-N4-ethyl-1,3,5-triazine-2,4-diamine | | 3.66 | 4.3 | 25 | 74 | herbicide, basic pesticide |

* – Pesticide Properties Data Base. Accessed 6 August 2019; n.r. – not reported; pK_a – dissociation constant, DT₅₀ – half-life in the soil

adsorption data (R^2 : 0.98, K_F : 0.69–1.49, $1/n$: 0.56–0.73) and the isotherms are as the L-type according to the classification of Giles et al. (1974). The values of estimated K_F parameter that characterizes the intensity of adsorption were higher for the soil with a higher organic carbon content and indicated that organic carbon was the main factor affecting CHL adsorption in the studied soils.

The adsorption of IPU on different soils and sediments have been the object of many reports (Coquet 2002, Ghafoor et al. 2013). In each study, adsorption data fitted well with Freundlich isotherm model. Estimated values of adsorption parameters for 14 soils from north France showed that the value of K_F was between 0.61 and 1.82 and $1/n$ was between 0.84 and 0.92 at R^2 : 0.9969–0.9996 (Coquet 2002). The value of $1/n$ could be related to the degree of heterogeneity of the soil adsorption surfaces. K_F values were correlated to organic carbon content and no significant correlation was found for $1/n$. The low $1/n$ values indicate a low affinity between the soil components and IPU. Moreover, the $1/n$ values classify these isotherms as type L, which indicates a decrease in specific adsorption sites with increasing concentration as the adsorptive sites become occupied.

Results of Ghafoor et al. (2013) showed the effect of depth of Sweden soil on IPU adsorption parameters. K_F values were significantly correlated with the mass fraction of clay and organic carbon.

Moreover, three-parameter model shows that IPU adsorption increased with decreasing pH. Vallée et al. (2014) investigated the soils of France and found a wide range of Freundlich coefficient (K_F) values from 0.70 to 20.48 and $1/n$ was <1 (0.66–0.82), R^2 : 0.73–0.99 in similar levels as in the above studies.

Ertli et al. (2004) observed a weaker adsorption of IPU at pH 8 than at pH 5. The presence of N-H groups in isoproturon molecule allows for the creation of hydrogen bonds between the O, N and H atoms of the IPU molecule and O and H atoms in surface functional groups in minerals and humic substances of soil under acidic conditions. Whereas in alkaline conditions the dissociation of the N-H bond in the isoproturon molecule gives a negative charge that is repelled by negatively charged particle surfaces.

Retention of CHL and IPU in different types of soil as a function of their physicochemical properties was investigated by ElGouzi et al. (2012). The Freundlich equation was considered suitable for the description of all isotherms obtained. On the basis of comparison of their K_F parameters, it was found that regardless of the type of soil used for adsorption experiments, IPU adsorption was lower than CHL adsorption. This dependence is a result of differences in the chemical structure of these herbicides. The 4-(1-methylethyl) group in IPU is a greater steric hindrance than the 4-methyl substituent present in CHL, which may decrease IPU adsorption in soil. On the other hand, the chlorine atom present in the CHL structure may increase the adsorption of this substance.

The obtained K_F values for IPU (0.64–10.14) and CHL (1.43–18.59) were in agreement with other reports.

In three of investigated soils, the IPU adsorption curve was of type C, with the coefficient $1/n$ in the range 0.99–1.20, which proved that the dominant mechanism of pesticide-soil interactions was the partition. In soils with the highest

conductivity $1/n$ for IPU followed an L-type isotherm (K_F : 0.62–10.14, $1/n$: 0.55–0.89).

El Arfaoui et al. (2012) investigated adsorption of IPU on 11 soil samples with different physicochemical characteristics. The obtained results indicated that the SOM and calcite content to OM ratio was the main parameter affecting IPU adsorption in calcareous soils. With an increase in SOM content in soils, a higher adsorption of pesticides was observed, while calcite inhibited this phenomenon.

Organophosphorus pesticides

Phorate is an organophosphorus insecticide and acaricide, which was used in agriculture and forests to control mainly chewing type insects. Chlorpyrifos is another member of organophosphate insecticide family used for foliar and edaphic applications (Rani and Juwarkar 2010).

Adsorption of phosphate to soil is favorably affected by the presence of OM and clay minerals. Due to the non-ionic character of phorate, as well as other phosphorous compounds, it is considered that the pH of the soil does not affect the adsorption of this group of pesticides in soil.

Electrophilic hydrogen phorate atoms form hydrogen bonds with HAs carboxylic groups, which was confirmed by Fourier transform infrared spectrometry (FTIR). On the other hand, van der Waals bonds are formed between silicates and cations of clay minerals and carbon, oxygen and phosphorus present in phorate structure (Chen et al. 2004, Rani and Juwarkar 2010).

The process of phorate adsorption on tropical soils (organic carbon content of 3.5–8.2%) can be described by Freundlich adsorption isotherms (R^2 : 0.82–0.92) (Chen et al 2004). The $1/n < 1$ (0.58–0.66) indicates a favorable adsorption. The values of K_F varied from 10–17. Whereas, the study of adsorption of phorate on vertisol (organic carbon content of 1.64%) showed that the experimental data could be fitted to both Freundlich and Langmuir equations, following the Freundlich isotherm (R^2 : 0.95) better than the Langmuir isotherm (R^2 : 0.90) (Rani and Juwarkar, 2010). The values of K_F and $1/n$ (Freundlich model) were found to be 1.94 and 0.35, respectively. Higher organic content in the tropical soils caused higher adsorption.

The value of $1/n < 1$ indicates that the adsorption process is favorable. The values of q_{max} and K_L estimated from the linear form of the Langmuir equation were 8.17 mg/kg and 0.062 L/mg respectively.

Chlorpyrifos is adsorbed on organic matter in soils and bottom sediments as well as on clay minerals. Chlorpyrifos adsorption on soil is positively influenced by organic carbon content. The desorption of this pesticide decreases with an increase of the initial concentration (Álvarez et al. 2013, Gebremariam et al. 2012). In field soils negative correlation coefficients were found between mobility factor (R_f) and content of SOM, clay, and CEC (Shao-nan et al. 2007). According to a literature review (Gebremariam et al. 2012), there is no unambiguous mathematical model describing the sorption-desorption process of chlorpyrifos in soil.

It is therefore difficult to predict the adsorption capacity of soils and sediments without knowledge about their mineral composition and organic matter content.

According to Gebremariam et al. (2012) the adsorption of chlorpyrifos was determined for about 28 different soils

of different pH varied from strongly acidic to moderately alkaline and with different organic matter content. Data was fitted with the Freundlich model and showed the value of $1/n$ varying from 0.77 to 1.83 and K_F from 18 (for Beverly soil and sand) to 1862 (for organic soil with organic matter content 75.3 mg/g) with a mean and median value of 653 and 553, respectively.

Organophosphate pesticides form stable complexes with the following metal ions: Co, Cu, Fe, Mn, Ni, and Zn commonly found in soil solution. These complexes are persistent and insoluble in water at typical environmental conditions (Kaur et al. 2017).

Chloroacetanilide pesticides

Butachlor is a non-ionic (except strong alkaline and acid conditions) hydrophobic chloroacetanilide herbicide. It is used to eliminate broad-leaved weeds and annual grasses. Its properties are presented in Table 1.

The adsorption and desorption experiments described in (Liu et al. 2013) were conducted on synthesized amorphous hydrated Fe oxides (AHOs Fe), black and latosol soil, both with and without AHOs coating. In all the adsorption experiments, the obtained isotherms of butachlor adsorption were non-linear ($1/n$: 0.75–0.98) in the whole range of equilibrium concentrations applied. During adsorption, butachlor was in the form of a neutral molecule, at pH in equilibrium solution ranging from 4.11 to 5.97. It may be therefore concluded that adsorption by inorganic soil components (clay minerals and Fe oxides) and SOM is the prevalent mechanism of interaction between butachlor and soil. At high concentration of butachlor, the hydrogen bonds between the pesticide and SOM were observed. It was also proved that the adsorption of butachlor on AHOs iron atoms was weaker in the presence of SOM. Probably it was caused by the occlusion of minerals by organic matter, thereby reducing their surface (Liu et al. 2013).

On the basis of the study of butachlor adsorption on eleven different soils, it was found that the following factors influence the effectiveness of this process: clay, total organic carbon, pH and CEC of soil (Liu et al. 2008).

The tested soils showed different adsorption affinity to butachlor, although in all cases adsorption was described by Freundlich's isothermal equation. Organic matter was the prevalent factor influencing the butachlor adsorption on soils, with inorganic fraction, such as clay, whereas amorphous sesquioxides, played a minor role in this process. For soils with low clay/OC ratio (below 60), the butachlor was mainly partitioned into soil organic matrix, in the opposite case the butachlor adsorption was mainly influenced by clay surface.

The interactions between soil minerals, SOM and butachlor as a function of butachlor adsorption was described in He et al. (2014). The sum of butachlor adsorption to the individual fractions of soil was greater than adsorption to the bulk soil. The most significant differences were observed in the soils with relatively high clay to soil organic carbon ratios. Therefore, it may be concluded that minerals physically protect favorable adsorption sites within SOM and thereby inhibit butachlor adsorption by influencing SOM physical conformation. The same conclusion was reached by Bonfleur et al. (2016), who compared the adsorption of butachlor on a series of soils with different total organic carbon (TOC) and recalcitrant (ROC).

These studies show that mineral soil significantly enhances the butachlor adsorption. On the other hand, the minerals may have negative indirect influence on butachlor uptake because of their effect on SOM structure during adsorption (He et al. 2014).

Ionic pesticides

Electrostatic attraction and surface complexation with iron and aluminum oxides present in soil are considered to be the main interactions responsible for the adsorption of ionogenic pesticides in soil. However, there are hardly any interactions between ligands and/or anions of pesticide and quartz or silica present in soil mineral layer. This is caused by the electrostatic repulsion of anions and negatively charged silica, neutral silanol groups (-SiOH) do not favor ligand exchange.

Based on the data provided (Vasudevan et al. 2002), it may be stated that among all soil components, iron and aluminum oxides and organic matter play a key role in the adsorption of ionic pesticides.

Acidic pesticides

2,4-D (2,4-dichlorophenoxyacetic acid) is a common synthetic auxin used in the control of broad leaf weeds. The 2,4-D adsorption tests on soil components (montmorillonite, humic acid and ferrihydrite) carried out by Celis et al. (1999) indicated that 2,4-D adsorption was high with S-type isotherm on ferrihydrite, moderate with L-type isotherms on humic acids and zero on montmorillonite.

Adsorption of 2,4-D on mineral soil was shown by Magga et al. (2012). The results of equilibrium batch experiments were used to estimate the parameters (K_F , $1/n$) of Freundlich isotherm ($1/n$ was 0.68) (Guo et al. 2000). Similar results were described in (Singh et al. 2014, Villaverde et al. 2008).

Soil mineralogy plays a crucial role in the 2,4-D adsorption on soils with high iron content, mainly in the form of hematite and goethite but also with γ -aluminum oxide. Little adsorption was observed on kaolinite (Vasudevan et al. 2002). Covalent and Coulombic interactions are prevalent mechanisms of anionic pesticides adsorption on soil. The efficiency of adsorption of organic anionic pesticides on iron and aluminum oxides depends on the pH of soil. In soils with low pH, higher adsorption of this group of compounds is observed than in alkaline soils, and the adsorption is most intensive near the pKa of individual pesticides. In alkaline soils there is a higher concentration of OH ions, which compete with pesticide anions for binding sites on the surface of inorganic oxides. For soils with low pH this is not the case (Vasudevan et al. 2002). According to more recent reports (Tunega et al. 2010), the hydroxyl groups on the surface of kaolinite and goethite are amphoteric, therefore under particular conditions the minerals may act as solid acid (base). The carboxylic group of 2,4-D forms multiple hydrogen bonds with surface hydroxyl groups, therefore the mechanism of interaction of this herbicide with hematite and goethite is similar. Moreover, surface complexation between -COOH group of 2,4-D and iron and aluminum atoms present in soil may enhance the adsorption of this pesticide (Vasudevan et al. 2002).

Ćwiela-Piasecka et al. (2018) undertook research on the adsorption of 2,4-D on two different types of organic adsorbents, HAs and biochar. HAs exhibited stronger affinity

for this herbicide than biochar. This is the result of specific interactions between 2,4-D and HAs functional groups. The high water-octanol partition coefficient ($\log P$) and the moderately hydrophobic character of biochar makes it difficult to create persistent interactions with polar 2,4-D, resulting in low adsorption of this herbicide.

Cationic pesticides

The quaternary ammonium pesticides paraquat (PQ) and diquat (DQ) are non-selective contact herbicides. Due to their wide spectrum of action they are used in the cultivation of many crop species. The chemical structure of PQ and DQ is planar. On the surface of the clay, PQ and DQ create a layer of uniformly oriented molecules, since the pyridinium ring of these herbicides may rotate. PQ is sorbed on all soil types and therefore makes it difficult to leach and biodegrade. Moreover, the strong adsorption of PQ and DQ to soils reduces their pesticidal power.

London interaction, van der Waals forces, hydrophobic adsorption and π - π interactions between this group of pesticides and soil components are responsible for their adsorption. The adsorption is stronger in the presence of clays because the C-H bond from the PQ methyl groups (Table 1) is able to form hydrogen bonds with oxygen atoms of the siloxane surface of silicate clays. Regardless of other factors (e.g. pH of soil, presence of negative charges on the surface of organic matter), the key factor influencing the adsorption of this group of pesticides is the presence of organic matter in the soil – with a decrease in the content of this component, the adsorption of cationic pesticides in soil increases as adsorption centers on the clay surface are not inhibited by the OM. Therefore, humification of organic matter has an influence on the physicochemical and biological properties of the organic constituents that may interact with residues of plant protection products (Boesten 2016, Maqueda et al. 1993, Pateiro-Moure et al. 2009). The dominant mechanism of this interaction are Coulombic interactions (in the case of interlayer spacings in montmorillonites and kaolinite) and van der Waals forces (in the case of kaolinite) (Pateiro-Moure et al. 2009).

Both DQ and PQ, as well as others bipyridilium pesticides bind to soil HS forming highly stable bonds with the carboxyl groups of the soil organic matter.

The best isotherm fits were obtained with the Freundlich equation (R^2 : 0.88–0.99, $1/n < 1$) (Pateiro-Moure et al. 2010).

Moreover, adsorption study of PQ and DQ on vineyard-devoted soils show the best fits for adsorption to soils were reached with the Freundlich equation, Langmuir fittings were not satisfactory. DQ behavior was similar to that of PQ and gave satisfactory fittings with Freundlich equation (R^2 between 0.94 and 0.99). The Freundlich coefficient K_F for PQ and DQ in soils was, respectively, >4000 , 2600–3500 and $1/n$ parameter was 0.22–0.31 and 0.19–0.26, respectively.

Adsorption studies of PQ on clayey components of soils were also conducted. PQ strongly adsorbed on a montmorillonite-rich material originating from the Hammam Bouhrara deposit (Maghnia, Algeria) in accordance with isotherm of H-type of the Giles classification (Sidhoum et al. 2013). The adsorption data very well fitted with Langmuir isotherm ($R^2=0.9999$). The maximum adsorption capacity of montmorillonite ranged from 77 to 111 mg/kg depending on

the temperature of the solution and its ionic strength. The Langmuir constant was from 1.5 to 2.17 L/mg.

Adsorption studies on illite as a soil component indicated that PQ adsorbed better according to Langmuir isotherm ($R^2=0.9998$) than to Freundlich one ($R^2=0.9757$). Estimated values of Langmuir isotherm were $q_{max} = 0.212$ mmol/g, $K_L=0.690$ L/mmol, whereas the values of Freundlich isotherm were $K_F = 0.217$ and $1/n = 0.064$ (Seki and Yurdakoç, 2005).

The influence of OM in decrease of PQ mobility is limited because dissolved organic matter may also interact with the herbicide and therefore have a positive effect on leaching. Moreover, PQ adsorption is affected by soil pH and the ionic strength of the soil solution. With the increase in pH there is an increase in the ionization of the surface acid groups of organic matter, which results in an increase in herbicide uptake, while at the same time there is an increase in the solubility of solid organic matter and an increase in the concentration of DOM (Gondar et al. 2012).

Basic pesticides

Triazine herbicides may be divided into two subgroups: chlorotriazines (e.g., atrazine and terbuthylazine), and triazines containing SCH_3 substituent (ametryn, terbutryn). The chemical structure of triazines, especially with substituents, which influence the alkaline character of nitrogen atoms and the acidity of N-H bonds, influence the character of herbicide – soil interactions. According to Chefetz et al. (2004), chlorotriazines undergo stronger adsorption and lower desorption in soil than triazines containing the $-SCH_3$ group as a substituent. This difference results from the possibility of creating hydrogen bonds between chlorotriazines and carboxylic groups of soil organic matter.

There are many reports concerning atrazine adsorption on soils and clay minerals. According to some of them this process can be described by Freundlich (Gao et al. 1998, Janoš et al. 2013) or/and Langmuir isotherms (Yue et al. 2017). Freundlich isotherm fitted very well the experimental data of adsorption atrazine on agricultural soils (R^2 : 0.970–0.998, $1/n < 1$) (Park et al. 2004), on clay minerals ($K_F=924.3$, $1/n < 1$) (Besse-Hoggan et al. 2009), and on sandy and clay loam soils ($R^2 > 0.91$, $1/n < 1$) Businelli (et al. 2000).

However, for adsorption on calcareous and agricultural soils ($R^2 > 0.99$) (Coquet (2002), Villaverde (2009)), on peat soils (Chappell et al. 2005) and bentonite (Wang et al. 2011) an estimated value of $1/n$ was found > 1 .

According to Yue and co-workers (2017) who have studied the adsorption of atrazine on the laterite, paddy and alluvial soil atrazine adsorption data was fitted well using Freundlich ($1/n$: 0.581–0.676, K_F : 1.855 (paddy soil) – 2.43 (alluvial soil) and Langmuir (K_L : 0.214 to 0.694 L/mg and q_{max} : 5.577 (paddy soil) – 15.898 (alluvial soil) mg/kg models.

Atrazine adsorption data for laterite and paddy soil was better fitted by the Freundlich model, which assumes that the adsorption occurs on a heterogeneous surface with the possibility of adsorption being multi-layered. The low values of K_F indicated that atrazine is probably highly mobile in soil. The Langmuir constant (K_L) showed the affinity of the soil surface for atrazine.

According to Barchanska et al. (2013) and Czaplicka et al. (2016) the interaction between atrazine 1,3,5-azidine ring and

SiO₂, the main inorganic components of soil, is the key reason of the long-lasting persistence of atrazine in soil (DT50: 108 days according to PPDB). Nano copper can increase the persistence of this herbicide in soil, what is the result of physical-chemical interaction with plant protection products (Parada et al. 2019).

The triazines interact both specifically (H-bonding and charge-transfer interactions) and non-specifically (hydrophobic-like interactions) with soil organic matter.

On the basis of H-NMR, differential thermal and FTIR analyses on the interaction of s-triazines with HS, it was found that between herbicide molecule and HS there may be even up to several H-bonds. These bonds occur between carbonyl groups of HS and secondary amino groups of s-triazines. HS content and acidity of soil are the key parameters determining the efficiency of adsorption of s-triazines in soil (Nearpass 1965).

Due to the directly proportional relationship between organic carbon adsorption coefficient of triazines and the octanol-water partition coefficient, it is claimed that not only hydrogen bonds between these herbicides and soil organic matter, but also hydrophobic partitioning-like interactions are responsible for the adsorption of these compounds in soil. It is noteworthy, however, that atrazine exhibits lower organic carbon adsorption coefficient ($K_{oc}=100$) values than other triazines (i.e. ametryn, terbutryn and terbuthylazine, 316–2432) (PPDB).

Based on IR research on s-triazines adsorption on HS, it was concluded that ionic bonding can occur between a protonated secondary amino-group of the s-triazine and a carboxylate anion (Senesi and Testini 1980). This type of bonding is influenced by the soil pH.

The high content of aromatic structures in the adsorbent favors the adsorption of atrazine, therefore, according to Kulikova and Perminova (2002), hydrophobic interactions are responsible for the adsorption of atrazine on SOM. On the other hand, Chefetz et al. (2003) reported that atrazine interacts also with aliphatic domains of SOM.

The shift towards lower frequencies in the atrazine IR spectra in the presence of HS is considered evidence of the formation of charge-transfer complexes resulting from interactions between methoxytriazines and SOM as shown by Senesi et al. (1987). This interaction leads to an increase in the free radical concentration (Senesi et al. 1987).

The carboxylic groups of SOM may act, depending on soil pH, as proton acceptor for the amino group or proton donor for the nitrogen atom of the triazine ring (Chefetz et al. 2004). The decrease in pH causes triazines protonation, promoting adsorption on organic matter and decreasing their herbicidal activity (Alletto et al. 2010). Moreover, according to Hong et al. (2019) atrazine is able to form solution-phase complexes with dissolved organic matter. This property of atrazine was confirmed by Shan et al. (2020). Based on the studies described in Gao et al. (1998), it can be concluded that under specific conditions an increase in soluble OM concentration increases the mobility of atrazine in the soil environment.

Not only organic matter influences the organic pollutants adsorption on soil, but also its granulometric composition (Pronk et al. 2013). Li et al. (1996) studied atrazine adsorption on soils of different granulometric composition (45–425 mm) and found statistically insignificant differences in atrazine adsorption depending on the size of the fraction. On the other

hand, Huang et al. (1984) conducted a similar research and found that atrazine was preferentially sorbed on the fine silt fraction (2–5 mm grain size), regardless of the type of soil (silty clay soil or loam soil).

Summary

Numerous studies on the mechanisms of adsorption and transport of pesticides in soils indicate that the principal factor influencing pesticide adsorption is the soil properties: content and chemical properties of soil organic matter (content of organic free radicals as well as phenolic, hydroxyl and carboxylic groups, aromaticity and humification degrees) as well as composition and physical properties (pH, CEC, granulometry etc.) of the inorganic layer. The complex mechanisms of interactions between pesticides and soil based on van der Waals forces, ionic and covalent bonding, ligand exchange and charge transfer complexes formation have also been demonstrated. It has also been shown that the nature of interactions is strictly dependent on the structure of the pesticide molecule, especially the presence of functional groups, and its physico-chemical properties.

Based on the related literature, the following overall conclusions on adsorption of pesticides in soil may be drawn: i) soil with well-humified HAs tends to create chemical bonds with sorbed pesticides, while soil with low humified HAs tends to interact with pesticides through hydrophobic interaction; ii) HAs exhibit higher affinity for charged pesticides than for neutral ones; iii) polar and semi polar pesticides are adsorbed to HAs by ionic and charge-transfer interactions as well as hydrogen bonding; iv) for hydrophobic pesticides the adsorption is considered as a partition between solution and SOM; v) the metal-pesticide complexes are stable and insoluble and thus accumulate in the environment – this phenomenon should be taken into consideration since most of the analytical methods for pesticide determination in soil are dependent on the solubility of these compounds.

Based on the results collected in this review about the mechanisms of interaction between pesticides with individual soil components, the results of this article may be employed to draw general conclusions on the behavior of other organic environmental pollutants in soil.

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