

## Chapter 8

# Sorption and desorption of agro-pesticides in soils

**Binoy Sarkar<sup>1</sup>, Raj Mukhopadhyay<sup>2</sup>, Asit Mandal<sup>3</sup>, Sanchita Mandal<sup>1</sup>, Meththika Vithanage<sup>4</sup> and Jayanta Kumar Biswas<sup>5</sup>**

*<sup>1</sup>Department of Animal and Plant Sciences, The University of Sheffield, Sheffield, United Kingdom, <sup>2</sup>ICAR-Central Soil Salinity Research Institute, Karnal, India, <sup>3</sup>ICAR-Indian Institute of Soil Science, Bhopal, India, <sup>4</sup>Ecosphere Resilience Research Center, Faculty of Applied Sciences, University of Sri Jayewardenepura, Nugegoda, Sri Lanka, <sup>5</sup>Enviromicrobiology, Ecotoxicology and Ecotechnology Research Unit, Department of Ecological Studies, and International Centre for Ecological Engineering, University of Kalyani, Kalyani, India*

### 8.1 Introduction

In intensive agricultural practices, the use of agrochemicals has considerably magnified in the last few decades (Yadav et al., 2015). Agro-pesticides are the most commonly used chemicals in agriculture and comprise insecticides, bactericides, and herbicides according to their functions. Based on the chemical structures, these chemicals include organophosphorus, organochlorine, nitrobenzene, phenol, metallo-organic, and numerous other compounds. Pesticides have several benefits in crop management, yield and material preservation, and minimizing pest–disease incidence by controlling harmful phytopathogens (Özkara et al., 2016). In modern agriculture the widespread application of agrochemicals may pose undesirable impacts on the soil ecosystem and groundwater quality (Racke, 2003).

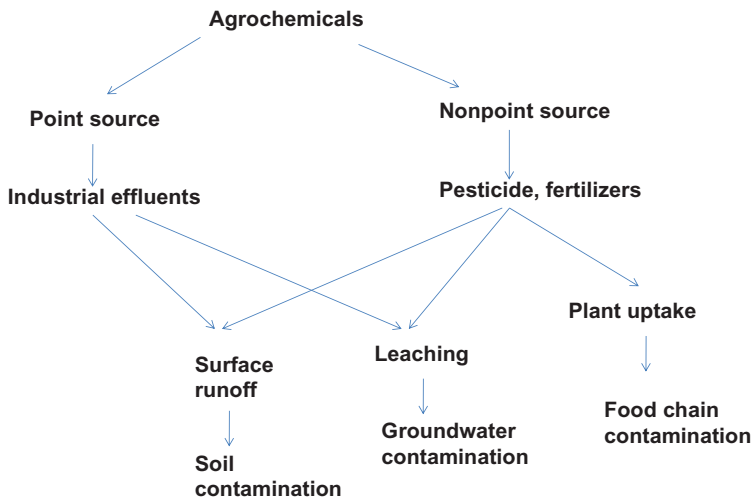
The agrochemicals and their residual products/mixtures may remain in the soil for quite a significant period of time (Gupta and Gajbhiye, 2007). The fate of pesticides and their interactions with the soil may confer a varying degree of toxicity, and their degradation products may exhibit many environmental limitations and food chain contamination including causing human carcinogenicity (Pehkonen and Zhang, 2002; Nakata et al., 2002; Qing Li et al., 2006). Soil contamination with agrochemicals can also impact the agricultural ecosystems by affecting the soil biota and their diversity responsible for biogeochemical cycling of nutrients (Feld et al., 2015).

The behavior of pesticides in soils strongly depends on their adsorption–desorption processes and is influenced by many pedological factors (Barriuso and Calvet, 1991; Weber et al., 2004). The toxicity and persistence behaviors of pesticides in the natural environment specially depend on their sorption characteristics. This phenomenon is important to predict the mobility and bioavailability of the agrochemicals in soils. Soil clay components have different reactive sites available for the sorption of pesticides and their transformation products. The applied fraction of pesticides in the soil may be attached to the soil colloids including mineral and organic particles and may remain persistent for a long duration. On the other hand, loosely bound pesticide molecules may desorb from the active sites into the soil solution and become bioavailable (Wu et al., 2011). A significant portion of applied pesticides, typically ranging from 20% to 70%, or their degradation products may remain in the soil as persistent residues bound to the soil colloids (Calderbank, 1989). In the colloid-bound state, these compounds are difficult to extract and characterize and tend to lose their biological activity to a considerable extent.

Sorption–desorption processes not only determine the transfer of pesticides in different environmental compartments such as soil, water, and air but also pose a significant impact on their uptake and metabolism by different microorganisms and plants (Konda et al., 2002). The accumulation of pesticides in different soil phases can be investigated by the nature of the soil components with different adsorption efficiency and by the physico-chemical properties of the pesticide molecules (Monkiedje and Spiteller, 2002). For example, clayey soils with amorphous mineral matters and organic matter can modify the pesticide sorption behavior. The present chapter focuses on various attributes controlling the sorption/desorption behaviors of pesticides in contaminated soils under different cropping systems and climatic conditions.

## **8.2 Occurrence of agro-pesticides in soils**

Soil is the biggest sink of pesticides applied for agricultural purposes, which potentially affects various components of the soil environment and ecosystem (Gill and Garg, 2014). The distribution and occurrence of pesticides as a mixture of multiple compounds in the soil depends on the seasonal variation of their applications in farming practices under various land use patterns. Many agrochemicals used in agricultural fields may pass into the soil by missing their intended target sites through surface runoff and subsurface leaching from the treated plants or by spillage during application (Fig. 8.1). Persistence and movement of these agrochemicals in the soil and their transformation products are determined by some parameters of the compounds such as water solubility, sorption–desorption phenomena, and half-life in soils. The pesticides and their residues are retained by soils to different



**FIGURE 8.1** Agrochemical contamination in the soil–water–plant systems.

degrees, depending on the interactions between soil and pesticide properties. The unwanted uptake of pesticide residues by crop plants may lead to the soil–food–human chain contamination.

Many of the agrochemicals, particularly pesticides, can be persistent in the soil for several decades (Table 8.1) and adversely affect the soil quality. Pesticide entry and accumulation occur in the soil via spray drift and wash off from treated foliage, and release from granulates or from treated seeds in the soil (Burauel and Baßmann, 2005). A number of pesticides such as soil fumigants and nematicides are directly applied to soils for controlling soil pests and plant diseases. The persistence of pesticides in the soil is generally greater than any other living systems by virtue of their metabolisms. Many soil physicochemical properties and biological and environmental factors control the mobility of pesticides and their transformation (Arias-Estévez et al., 2008). All these factors affect the sorption/desorption, volatilization, degradation, uptake by plants, and runoff and leaching of pesticide molecules. In the soil, several factors such as organic matter content, nature and amount of clays, soil minerals, soil pH, and soil temperature play critical roles controlling the behavior of pesticides (Hamaker and Thompson, 1972; Wauchope et al., 2002; Vryzas et al., 2007). The accumulation and formation of bound residues in the soil generally reduces the leaching, runoff, uptake, and bioavailability of pesticide molecules (Lerch et al., 2009). One of the most influential soil characteristics controlling pesticide mobility and transformation is the organic matter content. Soil organic matter (SOM) has much higher cation exchange capacity (CEC) than clays which can also form complexes with metals and organic compounds such as pesticides, sometimes

**TABLE 8.1** Half-life of various pesticides in soils.

Name of the pesticides	Half-life in soil
Dichlorodiphenyltrichloroethane	10–15 years
Endrin	12 years
Mirex	10 years
Polychlorinated biphenyls	10 years
Toxaphene	12 years
Dieldrin	5 years
Heptachlor	0.5–3.5 years
Chlordane	1 year
Diuron	90 days
Simazine	60 days
Pendimethalin	40 days
Dicamba	30–60 days
Sulfosulfuron	11–47 days
Methoprene	10–14 days
2,4-D	1–14 days
Pyrethrins	2.2–9.5 days
Capsaicin	2–8 days
Propachlor	4 days

rendering them immobile. The larger the organic matter content in the soil, the greater the adsorption of pesticides and the existence of bound pesticide residues. The capacity of the soil to hold positively charged ions in an exchangeable form is important with paraquat and other pesticides that are positively charged. The movement of agrochemicals or soil bound pesticide residues may occur from surface soil into the soil profile through dissolving in the runoff water and eventually reach to the groundwater (FAO, 2000). The transfer of agrochemicals in the soil profile and groundwater systems is also influenced by several hydro-climatological factors such as distribution of rainfall, soil drainage, depth of the groundwater, and of course the biodegradability and mobility of the pesticides. The agronomic management of crops, such as timing of sowing, amount and method of pesticide application, and the use of irrigation, and cover crops may influence the accumulation of pesticides in the soil (FAO, 2000; Wyman et al., 1985; Helling and Gish, 1986).

Soil pH is another important property controlling pesticide adsorption, and abiotic and biotic degradation processes (Burns, 1975). It influences the sorptive behavior of pesticide molecules on clay particles and organic colloid surfaces. Thus soil pH influences the chemical speciation, mobility, and bio-availability of the pesticide molecules (Hicks et al., 1990). However, the effect of pH would depend on the compound being degraded and the organisms responsible for the degradation too. Studies have shown a more rapid degradation of pesticides in soils with higher pH. Once residues bind through sorption in the soil, the microbial activity can be limited when pH remains between 8 and 8.5, and the biodegradation performs the best at a neutral pH (pH = 7). The adsorption of pesticides increases with decreasing soil pH for ionizable molecules (e.g., 2,4-D, 2,4,5-T, picloram, and atrazine) (Andreu and Picó, 2004). Furthermore, many pesticides can persist for long periods in the ecosystem; for example, organochlorine insecticides, paraquat, and diquat were detectable in the surface water even 20 years after their use had been banned (Larson et al., 1997).

The increasing use of pesticides serves as one of the major nonpoint sources of soil contamination (Sylvia, 2017). About 70% of the applied pesticides contribute to contamination of agricultural lands leaving residues (Sun, 2000). Among agrochemicals, the organochlorides (e.g., aldrin and dichlorodiphenyltrichloroethane) are considered the most dangerous, because after their application in the soil, they can remain in the environment for more than three decades, contaminating the entire ecosystem (Net et al., 2015). Many of these pesticides are considered as persistent organic pollutants that are typical organic compounds with high bioaccumulation, toxicity, and persistence in the environment.

There are several ways through which agrochemicals can contaminate the environment. One of the major sources of contamination of pesticide is through nonpoint source pollution or diffuse contamination and dispersion to different environmental compartments. The pesticide transformation and mobility include various processes such as volatilization, spray drift, wash and runoff, leaching, and lateral drainage, while pesticide degradation encompasses photolysis, and biotic and abiotic breakdowns. Environmental contamination by pesticides may also occur through dust during the seed treatment process. Moreover, plant materials are the carrier of pesticide residues that can be released into the soil during plant litter decomposition.

The occurrence of pesticides in soil is also controlled by the half-life of pesticides (Table 8.1), the magnitude of which is also controlled by various conditions (soil depth, region, season, etc.) (Vryzas et al., 2012). Soil temperature also affects the sorption and degradation processes of pesticides (Barriuso et al., 2008). It has been estimated that half-lives of pesticides in soil range over one order of magnitude under various conditions. Soil moisture affects sorption, leaching, and degradation of pesticides within the soil profile. In dry soil conditions, pesticide adsorption is greater, and microbial

activity is low. Although the abiotic processes contribute to the degradation of specific pesticides, biodegradation is the most studied dissipation process. Microbial community structure and activity play a primary role in the degradation of pesticides. Enhanced biodegradation has been reported for many pesticide classes after their repeated applications (Karpouzias et al., 2016). The biodegradation and accumulation of pesticides take maximum effect in the surface soil, while at depth the biotransformation rate declines due to the reduction of microbial activities because of limited supply of organic matter (food) in the subsoil (Veeh et al., 1996; Accinelli et al., 2001; Vinther et al., 2001).

### **8.3 Factors affecting fate and mobility of agro-pesticides in soils**

In soil, clay and organic matter encompass the solid surfaces, which are the interfaces between soil, air, and water. Through ion exchange and physical forces, agrochemicals can be concentrated at adsorptive surfaces, removed from the soil solution, and used up by plants. Sorption determines the transport, degradation, and bioavailability of a particular agrochemical applied in the soil system. Here, we discuss the effect of most important soil factors such as clay content, clay type, organic matter, and pH that mainly govern the fate of applied agrochemicals in the soil.

#### **8.3.1 Effect of clay types and contents**

The sorption of agrochemicals including pesticides and herbicides involves the interaction with mineral materials present in soils. The soil minerals are the central characters deciding the adsorption and release patterns of the agrochemicals onto the soils. The inorganic constituents of soil, predominantly the clay fraction, play a key role in pesticide adsorption (Baskaran et al., 1996). Soil clays are negatively charged, and they hold a large specific surface area (Sarkar et al., 2018). Consequently, soils high in clay content (fine-textured) have the tendency to adsorb more agrochemicals and generally possess a higher rate of adsorption than coarse-textured or sandy soils. Clay mineral surfaces are coated with metal oxides and oxyhydroxides in soils (Singh et al., 2016; Sarkar et al., 2018). Further, the presence of organic matter makes the mineral surfaces more hydrophobic, therefore, reactive to hydrophobic organic compounds (Sarkar et al., 2018). The consequences of interactions between soil components and agrochemicals are not fully understood and depend on the interaction mechanisms among soil constituents and on the nature of the agrochemicals. Interassociation between coated mineral surfaces, organic matter, and other soil constituents may block the sorption sites of mineral and organic matter surfaces. In such instances, surface retention of agrochemicals may become less onto the mineral fractions.

The adsorption or retention of pesticides is directly proportional to the content of clay present in soils. For example, acetochlor recovery (%) was much less (84%) in soil having high clay content (23.6%) than in soil (94%) containing less clay content (3.44%) (Durovic et al., 2009). Similarly, metolachlor retention in soils was also positively influenced by the clay content and type of soil mineral constituents (Kodesova et al., 2011). Clay interlayers and surfaces saturated with different mono and divalent cations such as  $K^+$ ,  $Na^+$ ,  $NH_4^+$ ,  $Ca^{2+}$ , and  $Mg^{2+}$  play an interesting role in pesticide adsorption. Among the most common exchangeable cations in soils, the  $K^+$ -saturated clay minerals (homoionic clays) show strong sorption characteristics to pesticides. This might be due to the weak hydration energy of  $K^+$ . The hydration energy for  $K^+$  is  $-314$  kJ/mol, smaller than that of  $Na^+$  ( $-397$  kJ/mol), whereas the corresponding values for divalent cations such as  $Ca^{2+}$  and  $Mg^{2+}$  are  $-1580$  and  $-1910$  kJ/mol, respectively. Weissmahr et al. (1999) measured the retention of 4-nitrotoluene to a mixture of homoionic  $K^+$ - and  $Ca^{2+}$ -saturated smectite and found that the adsorption increased with an increase in the fraction of  $K^+$ -clay in the mixture. Further,  $K^+$ -saturated smectite has a *c*-axis spacing of  $12 \text{ \AA}$  that enables a dominant organic pesticide adsorption onto smectite in the soil (Li et al., 2004). The charged sites of unhydrated smectite surface are normally hydrophobic in nature, therefore, may interact with nonpolar pesticides. Conversely, when smectites are saturated with strongly hydrated  $Ca^{2+}$  and  $Mg^{2+}$ , the hydration sphere of exchangeable cations may reduce the area of interaction, therefore, may result in poor adsorption interaction between the exchangeable ions and polar pesticides (Li et al., 2004). A study involving clays of Southern Spain having different mineralogical composition, granulometry, high  $Ca^{2+}$  content, and medium–low CEC and specific surface area found that these clays showed higher retention capacity for metalaxyl onto their surfaces due to electrostatic attraction than other fungicides used under Spanish conditions (Rodríguez-Liébana et al., 2016). The clay granulometry was identified as one of the important properties for metalaxyl adsorption (Rodríguez-Liébana et al., 2016). Similarly, metalaxyl and aromatic tricyclazole were adsorbed well onto natural stevensite clay originating in Morocco (Azarkan et al., 2016). Imazethapyr herbicide retention was also significant in a Vertisol of Morocco having high smectite clay content (Oufqir et al., 2017). The authors revealed that high smectite, CEC, and organic matter contents of soil played a significant role in herbicide retention. About 91% herbicide sorption variability was reported due to smectite clays and CEC of the soil (Oufqir et al., 2017). Thiazafurion interaction with homoionic montmorillonites indicated that thiazafurion adsorbed in the interlamellar space of the clay mineral, mainly by substitution of water molecules associated with the exchangeable cations through the carbonyl-amide groups and formation of H– bonds or water bridge between the  $-NH$  group of the amide and the basal oxygen of the montmorillonite (Cox et al., 2005). However, the illitic soil (54.9% illite)

clay adsorbed a higher amount of the herbicide than montmorillonite one, indicating that illite and montmorillonite may be present in soils in different forms leading to different adsorption capacities of pure minerals (Cox et al., 2005). The retention ability/strength of agrochemicals in soils is often represented by the soil/solution distribution coefficient ( $K_d$  value) of the agrochemical in question. The  $K_d$  values are also described as the soil sorption values of the target agrochemicals. As listed in Table 8.2, the  $K_d$  values for agrochemical sorption vary widely depending on the type of chemicals as well as soil factors. The higher the  $K_d$  value, the stronger is the sorption of a given pesticide compound in soils. Among the soil properties, pH, clay, and organic matter contents are reported to be the most correlating factors that influence agrochemical sorption and retention in soils (Weber et al., 2004).

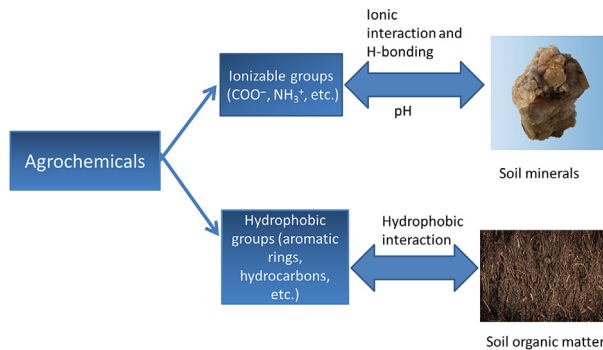
Like adsorption, degradation rate of agrochemicals also depends on the clay content in soils. The sorption rate of acidic herbicides increased when the clay content of soil increased from 3% to 66% and followed the order: dicamba < metsulfuron-methyl < 2,4-D < flupyrsulfuron-methyl-sodium (Villaverde et al., 2008). Thiazafurion, a polar uncharged herbicide, showed a decreasing trend of adsorption onto montmorillonite when the montmorillonite was coated with Fe(III)–OH species and revealed the opposite trend when iron was removed from the clay mineral (Celis et al., 1997). This suggests that the minerals and coatings alter the nature of surface of the clay

**TABLE 8.2** Mean  $K_d$  values of selected agrochemicals affected by soil factors.

Agrochemicals	Mean $K_d$ value	Most correlating soil factors
Rimsulfuron	0.87	pH
Quinclorac	1.24	Organic matter
Flupyrsulfuron-methyl	0.37	pH, organic matter
Propiconazole	6.27	Clay
Carbaryl	1.63	Clay and organic matter
Fenuron	0.76	Organic matter
Phorate	6.47	Organic matter
Tricyclazole	23.0	Clay
Thiabendazole	9.55	pH, organic matter and clay
Propargite	107	Organic matter
Bensulfuron	7.47	pH

Source: Modified from Weber, J.B., Wilkerson, G.G., Reinhardt, F.C., 2004. Calculating pesticides sorption coefficients (Kd) using selected soil properties. *Chemosphere*. 55, 157–166.





**FIGURE 8.2** Interplay of agrochemical and soil properties in the sorption and retention of agrochemicals in soils.

adsorbent. Therefore association between different soil constituents may determine the sorption behavior of soil aggregates (Celis et al., 1997). The mechanisms of pesticide adsorption onto soil clays are mostly hydrophobic interaction between organic compounds and clay minerals. Besides, proton transfer/hydrogen bonding and pH of the soil medium also play important roles in the retention of pesticides/herbicides onto the silicate minerals (Fig. 8.2). Hydrogen bonding (or proton transfer) and hydrophobic bonding were proposed to interpret the results of the interaction of atrazine with a podzolic soil (Davies and Jabeen, 2003). It was also reported that the surface of kaolinite contributed to atrazine hydrolysis (Davies and Jabeen, 2003). Wang and Keller (2009) studied the sorption/desorption behavior of atrazine using four soils and their clay, silt, and sand fractions. The authors concluded that the clay fraction was the most significant in atrazine retention, and a hysteresis effect was observed due to microporous structure of the clay minerals (Wang and Keller, 2009).

### 8.3.2 Effect of organic matter content

Like soil clays, SOM content is one of the most important factors that determine the fate and retention of agrochemicals applied to soils. SOM is considered as the primary adsorbent of nonionic pesticides. Therefore, it determines the concentration of such pesticides in the soil solution and regulates their transportation through the soil profile. The pesticides/herbicides can be adsorbed by organic matter itself present in the soil. Therefore SOM is one of the main rates controlling factors for agrochemical application in soils. The developed charge on the active sorption sites of SOM determines the adsorption of pesticides due to ionization of carboxylic groups present on the surface of SOM. Recently, Bt toxins are reported to interact with SOM due to its high specific surface area and CEC (Zhou et al., 2018). However,

the rate of application of pesticides holds a positive proportional relationship with the SOM content. If a land has soils containing varying amounts of SOM, the pesticide application rate is selected based on the adsorption maxima of the soil. This indicates that the probability of leaching loss of pesticides is high in fields that are poor in SOM content. This may result in the contamination of the groundwater (Fernandez et al., 1988). However, soils containing SOM > 5% directly influence the pesticide adsorption in soil, but the nature of organic matter shows little influence on the pesticide adsorption (Bekbolet et al., 1999). In contrast, humic substances are more stable and constitute the bulk of SOM in most soils. Humic substances are rich in stable free radicals, which play key roles in polymerization and depolymerization reactions and in the reaction with other organic molecules, including pesticides and pollutants (Sadegh-Zadeh et al., 2017). In general, high SOM content indicates that the soil is rich in organic carbon content; therefore partition coefficient of the pesticide should be based on organic carbon content ( $K_{OC}$ ) that gives a better picture of pesticide adsorption in soils. The variation in  $K_{OC}$  values of pesticides observed in different soils suggests the variation in the aromatic components of SOM. A highly significant positive correlation between aromaticity of SOM and  $K_{OC}$  values of nonionic pesticides such as carbaryl and phosalone revealed that the aromatic component of SOM is a good indicator of a soil's capacity to adsorb such nonionic pesticides (Ahmad et al., 2006).

Dissolved organic matter (DOM) plays an important part for pesticide adsorption. DOM content has both positive and negative effects on pesticide adsorption depending upon the type and functional groups present in the agrochemical molecules. Pesticides, which interact with organic matter, react with both the soluble and solid-phase fractions; therefore, competitive effects, the reversibility of these two types of interactions, and mass action effects then govern the partitioning of pesticides between the solid and soluble phases of the organic matter. For example, atrazine sorption increased with an increase in DOM content in the soil; conversely, 2,4-D and chlorpyrifos showed an opposite trend (Ben-Hur et al., 2003; Li et al., 2005). Senesi et al. (2001) reported an increase in pesticide sorption in soil amended with organic matter. The authors revealed that a higher sorption of alachlor, imazethapyr, and rimsulfuron occurred in the soil amended with sewage sludge, and multiple binding mechanisms such as H-bonding, ionic bonds, and charge-transfer bonds were responsible for the sorption (Senesi et al., 2001). Besides, the polarity and molecular weight of pesticides also play an important role during the interaction with soluble form of SOM. A positive correlation between napropamide and humic substances (humic and fulvic acids) was reported by Lee and Farmer (1989). They concluded that the association of napropamide with humic acid was stronger than fulvic acid, which indicated that the source of the DOM should also be considered during the herbicide adsorption studies. The sorption mechanisms of nonionic compounds

such as napropamide onto SOM include similar mechanisms as mentioned earlier. [Sadegh-Zadeh et al. \(2011\)](#) revealed that napropamide adsorption was very low in a sandy soil having negligible amount of SOM. Therefore, napropamide could move downward with the movement of water and might contaminate the groundwater. Soils that have high clay and SOM contents may show high retention capacity toward napropamide, hence, reduce its mobility through the soil profile. Therefore environmental contamination, including the groundwater and surface water, could be minimized after napropamide application via organic amendments. In contrast, literature revealed that MCPA (4-chloro-2-methylphenoxyacetic acid), an acidic herbicide usually used in paddy fields (Ferrasol), had a small Freundlich coefficient ( $K_f = 0.85\text{--}4.2$ ) in the presence of DOM, which indicated that the desorption of the agrochemical was dominant during the interaction between MCPA and DOM ([Wu et al., 2018](#)). The authors explained that DOM coating changed the soil surface properties, which consequently altered the interaction of the agrochemical with soil particles. Experimental data indicated that an organic acid resulted in low sorption of MCPA by conferring competitive sorption with DOM in the soil, and an increased solubility of MCPA was thus observed in the presence of DOM ([Wu et al., 2018](#)). In another study, the sorption behavior of atrazine, isoproturon, and paraquat was found to be controlled by the solid-state soil components, and DOM showed small effect ([Spark and Swift, 2002](#)). The sorption of 2,4-D was little affected by DOM in the soil because of noncompetitive adsorption with the soluble fractions of SOM ([Spark and Swift, 2002](#)). In contrast, higher mobility of atrazine and 2,4-D occurred when DOM concentration was quite high ([Spark and Swift, 2002](#)). Therefore, the transport of such pesticides through the soil profile may occur due to soluble complex formation between DOM and pesticides.

### 8.3.3 Effect of pH

Besides soil clays and SOM, pH governs the adsorption–desorption process of applied agrochemicals in soils. Soil pH has been shown to influence the sorption of many ionizable pesticides. Selected pesticides may exist in the soil solution as neutral, positively charged, or negatively charged species within the experimental pH range. Depending on pH, carboxyl and phenolic groups of SOM may be protonated/deprotonated, creating a net charge on the surface of the SOM. Soil pH influences the adsorption of agrochemicals in particular when they are dissociated or protonated within the studied pH range of the soil. The comparison of soils showing wide range of pH generally provides a picture of the behavior of an organic compound and reveals multiple results, mechanisms, and fates of agrochemicals. For example, [Sheng et al. \(2005\)](#) found that bromoxynil was dissociated at high pH to form anionic species. The adsorption of the anionic species was reduced on

the soil at pH 7.0 as compared to an acidic pH, which might be due to a reduced partition of the anionic species of bromoxynil onto SOM (Sheng et al., 2005). Conversely, ametryne in its molecular form was adsorbed at pH 7.0 by the soil through partitioning onto the SOM (Sheng et al., 2005). The protonated form of ametryne at pH 3.0 was substantially adsorbed by the soil primarily through electrostatic attraction (Sheng et al., 2005). However, statistical relationships between agrochemical sorption and soil pH do not always give a true picture of correlation under varying soil types. For example, Weber et al. (1986) did not find a significant relationship between pH and the adsorption of fluridone in 18 different soils of a pH range between 4.4 and 8.1 ( $r^2 = 0.10$ ). However, fluridone adsorption increased by about 38% and 42% due to a decrease in soil solution pH from 6.4 to 3.5 (Weber et al., 1986).

The impact of pH on the adsorption of ionizable pesticides has been reported in many studies, and this is controlled specially by soil compositions and characteristics of the agrochemicals. The pH dependence of sorption originates from the amount of ionic and neutral portion of pesticides existing at a particular pH level. However, this is applicable when pH is greater than the  $pK_a$  value of the compound. Soil colloids, mainly SOM and Al/Fe oxides, greatly influence the pH-dependent charge governing the electrostatic attraction or ligand exchange to adsorb agrochemical molecules. Similarly, organic colloids have strong pH-dependent charge that governs the degree of ionization of humic acid groups. Phenolic and alcoholic groups ( $pK_a$ ) of organic compounds remain nonionized under neutral pH, while ionized carboxylic groups ( $pK_a = 5.2$ ) are expected to coexist. For instance, Walker et al. (1989) measured the sorption and degradation rates of chlorsulfuron and metsulfuron-methyl in soils. It was found that the sorption of both the herbicides was inversely correlated with the soil pH and positively correlated with SOM (Walker et al., 1989). It was suggested that the soil pH was the primary controlling factor for herbicide sorption in most soils. Chlorsulfuron and metsulfuron-methyl have  $pK_a$  values of 3.8 and 3.3, respectively. Hence, these herbicides mostly exist under acidic conditions. Picloram sorption was also influenced by the pH and  $pK_a$  values of the organic compound. A significant amount of picloram sorption onto humic and humin acids was observed when the pH of the medium was close to its  $pK_a$  value, that is, 3.4 (Nearpass, 1976). A small unit change of pH along with the ionic strength resulted in a significant increase in the neutral fraction of the herbicide (Nearpass, 1976). The herbicide 2,4-D, an acidic pesticide, can remain in its molecular and anionic forms in soils. As the  $pK_a$  value of 2,4-D is very low (2.8), it exists in anionic form in the pH range common to variable-charge soils. Hence, its adsorption may occur on positively charged soil minerals. Positively charged hydroxides of Al/Fe of soil compounds thus show a high sorption capacity toward phenolic acids such as 2,4-D (Huang et al., 1977). This is attributed to the large chemical reactivity

of these positively charged minerals toward the negatively charged carboxyl and phenolic hydroxyl groups of 2,4-D (Huang et al., 1977). Similarly, the influence of pH and SOM on the adsorption of nonionic fungicides such as metalaxyl and penconazole was studied. The adsorption data fitted well to the Freundlich isotherm model (Gondar et al., 2013). It was reported that at  $\text{pH} > 5$ , partitioning of the fungicides between the solid phase and the soil solution was insignificant with respect to pH, while at lower pH range, the fraction adsorbed on the solid phase increased (Gondar et al., 2013). This phenomenon could be explained by the effect of pH on the ionization of carboxylic groups of SOM and hydrophilic nature of SOM (Gondar et al., 2013). The herbicide adsorption onto a volcanic soil under the influence of pH revealed that the maximum amounts of fluroxypyr, triclopyr, picloram, and clopyralid adsorbed were 75.2%, 69.7%, 40.5%, and 11.7%, respectively, at pH 4.0 (Palma et al., 2015). These results suggest that pH of the soil medium and acidic nature of herbicides can strongly determine the availability and leaching tendency of the agrochemicals through the soil profile (Palma et al., 2015). Therefore soil pH indirectly influences the environmental quality by controlling the movement, retention, and degradation of agrochemicals applied to the soil.

## 8.4 Conclusion

Agrochemicals are widely used in agriculture to manage pests and phytopathogens. Hence, it is very pertinent to study the fate and behavior of applied agrochemicals in soil. The important factors that affect the persistence of such agrochemicals such as clay type, clay content, SOM, and pH of the system are described in this chapter along with the mechanisms of retention in soil. Long-term persistence of agrochemicals is harmful for succeeding crops grown in the soil as they leave residues that may enter into the animal and human food chain. Many of the agro-pesticides exist in the soil environment as a mixture. Currently our knowledge about the fate and behavior of agro-pesticide mixtures in the ecosystem is inadequate. Therefore, research is needed in the future to address the issue of agro-pesticide mixtures in the soil–plant systems under various agro-climatic conditions.

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