

# Sorption/Desorption, Leaching, and Transport Behavior of Pesticides in Soils: A Review on Recent Advances and Published Scientific Research



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**Abstract** Pesticides are chemical compounds designed to be used as plant protection products (PPPs). They are applied in the field for the protection of plants against pests, weeds, and several diseases that affect and decrease the quantity and quality of agricultural crop products. After their environmental release, these synthetic substances undergo a variety of abiotic and biotic processes which determine their distribution in the environmental compartments, and consequently their fate and persistence. Sorption, desorption, and leaching are some of the processes that are included among the most important transportation pathways. Due to their extensive

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application and their potential ecotoxicological effects, the global scientific interest focusing on the research of the environmental fate and behavior of pesticides after their entrance in the environmental matrices is undiminished. The present chapter is a review of the recent scientific literature regarding the recent research on the fate of pesticides in soil regarding the processes of sorption/desorption and leaching. Based on the gathered information derived from the reviewed articles on the subject published in the last 5.5 years (from 01/01/2016 to 30/06/2021), useful conclusions and observations are reported about research trends. Furthermore, knowledge gaps in the current research are highlighted and suggestions for future research on this topic are also discussed.

**Keywords** Desorption, Environmental fate, Leaching, Organic micropollutants, Persistent organic pollutants, Pesticides, Soil distribution, Sorption, Transportation

## 1 Introduction

A wide variety of anthropogenic compounds with organic nature that are synthetic compounds produced for multiple purposes or applications are extensively used worldwide, such as personal care products, drugs and medicines, pharmaceuticals, plastics and polymers, dyes, solvents, endocrine-disrupting compounds, and several others. Pesticides, also known as PPPs, are also included among this long list of persistent organic pollutants (POPs) which are characterized as potential toxicants toward nontarget organisms.

More specific, the term pesticide is used for substances designed to be applied as PPPs against various pests, weeds, and diseases that are harmful to cultivated plants, and consequently threat and affect the crop yields. Their molecules are characterized by different physicochemical properties, mobility, bioavailability, and toxicity.

Concentrations of pesticides have been detected and measured in numerous environmental samples such as soil [1], surface water [2, 3], groundwater [4], sediment [2, 3], edible cultured fruits, vegetables, and agricultural products [5, 6]. In a recent study of Zhang et al. [3] investigating the occurrence of five target neonicotinoid insecticides in soil-water-sediment systems of urban and rural areas in South China the concentration levels of reported results were within the range of 0.003–229 ng g<sup>-1</sup> (dry weight, dw), 7.94–636 ng L<sup>-1</sup>, and 0.017–31.3 ng g<sup>-1</sup> (dw) for soil, water, and sediment samples, respectively. According to a different study of Pico et al. [6] the pesticide residues of 15 compounds (mainly insecticides and fungicides) out of a list of 62 substances belonging to a wide variety of chemical classes were detected in fruits from Saudi Arabia, whereas in 20% of the samples the detectable concentrations were above the maximum residue limits (MRLs). The results of a survey conducted by Zambito Marsala et al. [4] revealed the presence of seven pesticides (chlorantraniliprole, dimethomorph, fluopicolide, metalaxyl, penconazole, and tetraconazole) in 30% of the studied wells (situated in the Tidone

Valley, Province of Piacenza, North-West of Italy) at a level higher than  $0.1 \mu\text{g L}^{-1}$  that is the Environmental Quality Standard (EQS) for groundwater.

Based on the relevant published scientific literature, the occurrence, distribution, and persistence of those POPs in the ecosystems is a subject on which the interest of the global scientific community is focused undiminished. Therefore, the aim of the present study is to carry out a review concerning the scientific articles published within the last 5.5 years (from 01/01/2016 to 30/06/2021), regarding the research of the environmental fate of pesticides in natural soil samples and under different environmental conditions.

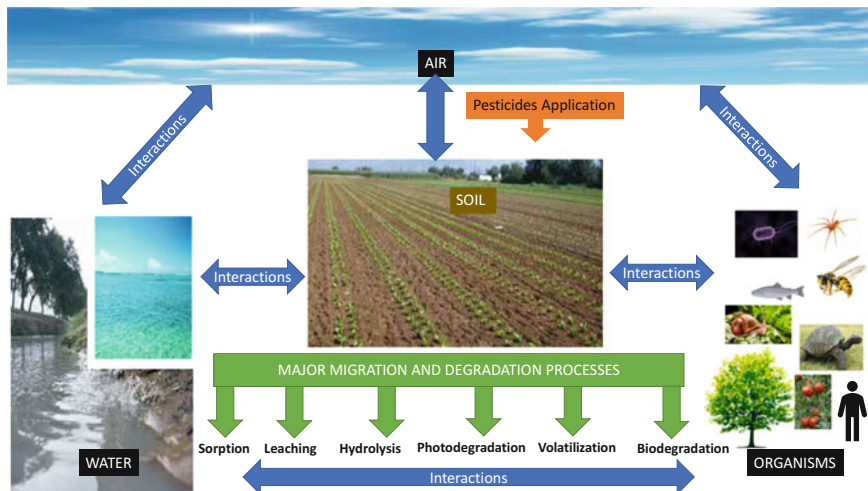
In more details, the current chapter provides a review of pesticides and selected transportation and distribution processes, which take place into soil environments and therefore determine the bioavailability and persistence of the selected molecules into field systems. The first section provides general data about the topic of discussion, i.e., pesticides classification, pathways of their entry into terrestrial matrices, and interactions between different environmental compartments. Subsequent sections discuss selected migration and mobility mechanisms on which the global scientific research interest has been focused. Particularly, the studies focusing on the phenomena of sorption/desorption and leaching are reviewed, and their main findings are summarized.

## 2 Pesticides in Soil Samples

An expansive range of synthetic pesticides belonging to different chemical classes, possessing diverse physicochemical properties, and targeting to multiple and dissimilar pests are available in the market. Those compounds are mainly used in agriculture and applied in the cultured fields.

Based on the criteria of their chemical structure pesticides are subdivided into categories of anilides, amides, organophosphates, organothiophosphates, carbamates, benzothiazoles, triazines, neonicotinoids, organochlorines, and many other chemical classes. The classification of pesticides based on their target organisms includes the classes of acaricides, fungicides, herbicides, insecticides, nematocides, and plant growth regulators. According to the World Health Organization (WHO) the classification of pesticides, based on their hazard towards exposed organisms, contains five classes which are: extremely hazardous (Class Ia), highly hazardous (Class Ib), moderately hazardous (Class II), slightly hazardous (Class III), and unlikely to present acute hazard (Class U) [7].

The introduction of pesticides into the environment takes place mainly through agricultural and urban applications of disease vectors control. Once in the soil, pesticides can enter aquatic environmental bodies through alternative pathways. The main phenomena that are responsible for the mitigation of pesticides are diffuse processes, surface runoff, leaching, erosion, spray-drift, and atmospheric deposition after their volatilization [8, 9].



**Fig. 1** Major migration and degradation processes to which pesticides substances are subjected to after their application in the field and interactions between other environmental compartments

As shown in Fig. 1, possible transfer and distribution of pesticide compounds between soil, water, air, and biota matrices occur while the extent of each interaction and exchanging phase phenomenon is affected by several parameters, which in turn are simultaneously dependent on: (1) the molecule and its physicochemical properties, (2) the characteristics of the environmental substrate that contains the pesticide, (3) the application practice in terms of method, pesticide load, frequency, time season, and other factors, (4) the environmental conditions such as temperature, wind, etc., and finally (5) the geological and climatic characteristics of the site of the application [10, 11].

After entering the environmental matrices, they go under chemical, (direct/indirect) photochemical, or biological degradation processes that are possible to take place concurrently with other physical phenomena that determine their removal and distribution into different environmental substrates, such as adsorption, evaporation, and surface movement [9].

Data concerning the major factors affecting the environmental fate and persistence of a pesticide are detailed in Fig. 2. Consequently, due to their unquestionable occurrence in residual quantities contained in various natural matrices and the potential ecotoxicological impacts increased scientific concerns have been raised.

In the subsequent sections, some of the main distribution and degradation pathways that determine the fate of pesticides in soil-water systems are discussed and the most important results of reviewed bibliography are summarized and presented.

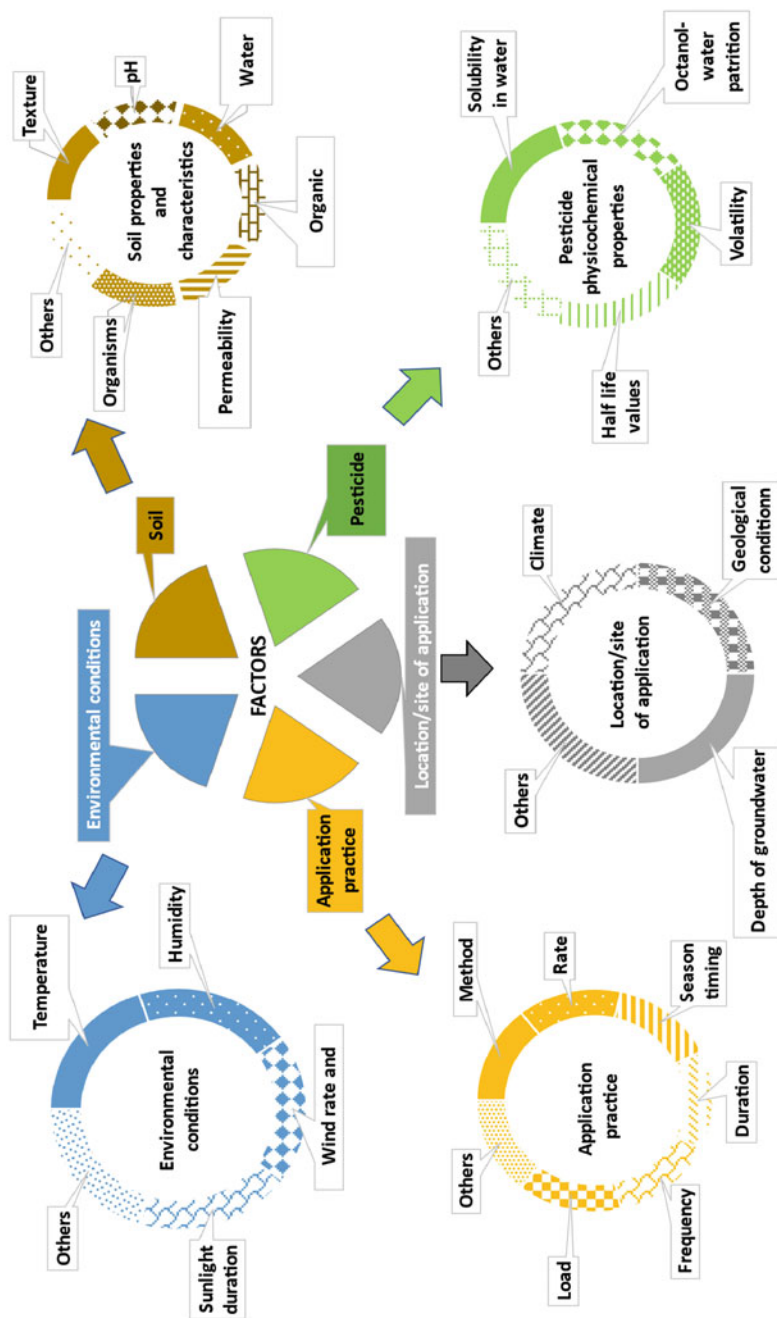


Fig. 2 Principal factors that affect the environmental fate of pesticides [Adapted from Pietrzak et al. [10], after Perez-Lucas et al. [11] and modified]

## 2.1 Sorption on Soil

Sorption of organic pesticides' molecules onto the solid phase constituents of soil (such as clay minerals, organic matter (OM), oxides and hydroxides of aluminum and iron) is one of the most important and primary processes that can occur either via a reversible or a non-reversible mechanism and therefore influence the amount of the pesticide that remains mobile in soil-water systems or not. When present in the soil many pesticides are bound to soil colloids (clay, OM), and consequently become less readily available to plants than the molecules that are not adsorbed and continue to move in the soil solution.

Several reviews, overviews, and meta-analysis studies on the sorption of pesticides among other POPs have been published in the past few years [8, 10–19]. According to the conclusions and findings of all published review works, the general agreement that sorption of pesticides by soils has been stated and reported.

Moreover, according to the findings of the present review in the same period of the last 5.5 years (2016–2021), a large number of modeling studies dealing with the pesticides transport and mobility in soils, leaching risk assessments, sorption data (such as adsorption constants  $K_{oc}$ ), subsurface fate and dynamics have been published [20–34].

Numerous theoretical and empirical sorption and desorption isotherm models have been used for the kinetics of the studied processes. Undoubtedly, (ad)sorption and/or desorption isotherms are frequently described by linear and nonlinear models among which Freundlich, Langmuir, Elovich, and Henry isotherm adsorption models are included which fit well the acquired experimental data. In Eq. 1 the logarithmic Freundlich model is described:

$$\frac{x}{m} = C_s = K_F * C_e^{1/n} \quad (1)$$

where  $K_F$  is the Freundlich equilibrium constant (usually in  $\mu\text{g}^{(1-1/n)} \text{mL}^{1/n} \text{g}^{-1}$ ),  $C_e$  is the concentration of the selected and studied pesticide (usually in  $\mu\text{g mL}^{-1}$ ) after the equilibration,  $C_s$  is the concentration of the (ad)sorbed pesticide in soil matrix ( $\mu\text{g g}^{-1}$ ), and finally  $1/n$  is the linearity degree.

With the condition that the adsorption of pesticides' reactive groups over the soils' particulates proceeds through a homogeneous distribution onto the adsorbents' surface and that no later interactions occur between adjacent adsorbed molecules that occupy a single surface site, the Langmuir adsorption isotherm can be applied which is described by the mathematical formulations of Eqs. 2 (nonlinear form) and 3 (linear form):

$$q_e = \frac{K_L * b * C_e}{1 + b * C_e} \quad (2)$$

$$\frac{C_e}{q_e} = \frac{1}{K_L * q_m} + \frac{C_e}{q_m} \quad (3)$$

where  $q_e$  and  $K_L$  are the concentration of adsorbed pesticide and the adsorption equilibrium constant, respectively, whereas  $q_m$  and  $C_e$  are the maximum adsorption capacity and the concentration of the pesticide compound in soil-water system, correspondingly after the equilibration.

A multilayer adsorption is described by Elovich's model that is expressed by the mathematical expression of Eq. 4:

$$\frac{q_e}{q_m} = b_e * C_e^{-\frac{q_e}{q_m}} \quad (4)$$

Among the several main mechanisms that have been proposed to explain the adsorption of pesticides onto the soil colloid components, van der Waals force attraction (dipole–dipole interactions), hydrophobic bonding, hydrogen bonding, charge transfer (electrostatic attraction), ion exchange, and ligand exchange mechanisms are included. Depending on the nature and physicochemical characteristics of pesticide molecules and soil constituents (acidity or basicity, solubility, charge distribution on the molecule, polarity, molecule size, polarizability, etc.) simultaneously mechanisms may occur [14, 15, 18, 30, 32].

## 2.2 Leaching in Soil

Frequently, the movement of solute pesticides occurs through the soil profile by the effect of water, rainwater, or irrigation water. In this way, the vertical transportation of several pesticides into the soil column by runoff is often observed and the removal of those molecules from topsoil into lower subsoil depths takes place. This process is known by the term leaching and via this phenomenon, the downward migration of organic pollutants through the unsaturated zone to groundwater is possible to happen. Therefore, the potential displacement of organic pesticides from the soil surface and root zone to aquifers which are consequently vulnerable to pollution toward pesticides used in crop production is a subject on which the scientific interest has been focused.

Diffusion and mass flow phenomena that take place simultaneously may be involved in the leaching process of pesticides through soil in the solution phase. According to the published scientific literature, numerous models have been developed and evaluated that describe the leaching of organic pesticides in the root zone and the intermediate vadose zone, and the flushing of residual solute mass in the aquifer [25, 32, 33].

### 3 Results and Discussion

#### 3.1 *Overview of Found Data Published in the Last 5.5 Years Regarding the Transportation Behavior of Pesticides in Soils*

The search was based on “Scopus Database” using as keywords the terms “pesticide,” and “soil,” and “sorption” or “desorption” or “leaching” process. Only original research publications since 2016 were considered, while all critical reviews and overviews published in the same period were excluded. Target pollutants are tested either individually or in mixture with other toxic pollutants.

Numerous scientific publications have arisen by researchers in the last 5.5 years concerning the investigations on the distribution and mobility of pesticides into soil compartments after their entrance into the field. More specific, during the current overview a great number of publications, overall 228 reports retrieved by “Scopus Database” have been found for the period 2016–2021 (during 01/01/2016 to 30/06/2021) regarding several different pesticides that belong to a wide variety of chemical families and have been investigated for their efficiency to be (ad)sorbed, desorbed on soils, and transported into groundwater.

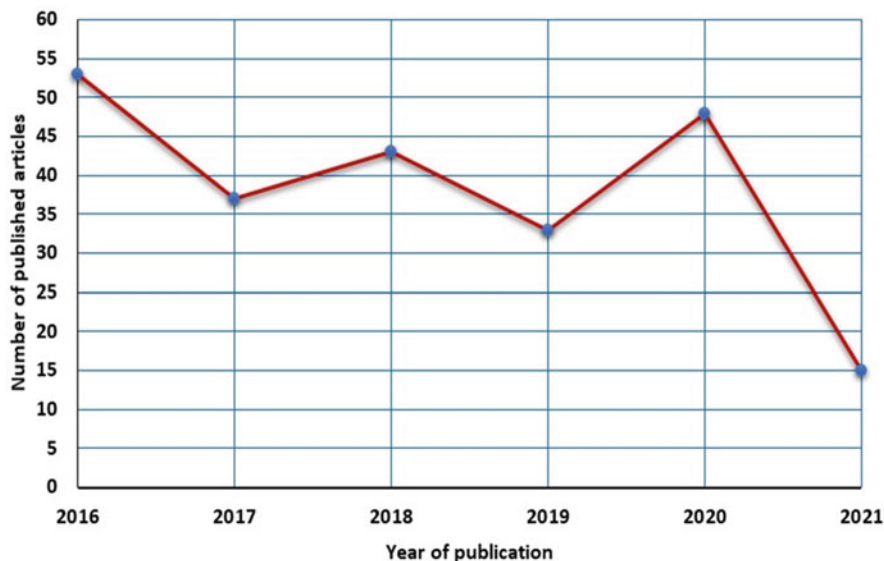
The annual number of records published for each year overviewed on investigating the (ad)sorption, desorption, and leaching processes of pesticides in natural soil substrates is illustrated in Fig. 3. In this point it must be underlined the fact that the survey for 2021 is restricted only to the first half of the year (from 01/01/2021 to 30/06/2021) that explains the low number of findings. In general, a slightly variable annual number of scientific published data regarding the theme is noticed that approaches the mean value of 40 reports per year (Fig. 3).

Table 1 provides a summary of all the 228 reviewed published data found during the present review work for each individual pesticide compound reported. The search was based on “Scopus Database” using as keywords the terms pesticide, soil, and sorption or desorption or leaching process. Only original research publications since 2016 were considered, while all critical reviews and overviews published in the same period were excluded. Target pollutants are tested either individually or in mixture with other toxic pollutants.

According to the findings of the current review it is observed that among the overall 186 individual pesticides for which evaluation of adsorption/desorption capacity on soil, leaching, and transportation process has been surveyed the triazine herbicide atrazine is the one on which scientific interest has been focused (24 reviewed articles, Table 1), followed by the organophosphorus insecticide chlorpyrifos (21 reviewed articles, Table 1), the nicotinoid insecticide imidacloprid (15 reviewed articles, Table 1), the organophosphorus insecticide glyphosate (13 reviewed articles, Table 1), and the systemic fungicide metolachlor (13 reviewed articles, Table 1).

Hence, it can be stated that the scientific interest has been focused on the most commonly used and frequently detected pesticides or/and the pesticides exhibiting





**Fig. 3** Annual number of records published during the period from 01/01/2016 to 30/06/2021 regarding the (ad)sorption, desorption, and leaching processes of pesticides into soil/water systems. The plotted data have been located by “Scopus Database” by entering the keywords “pesticide,” and “soil,” and “sorption” or “desorption” or “leaching”

the longer half-lives that can remain in soil at levels above several hundreds of  $\mu\text{g kg}^{-1}$  and therefore pose a higher ability to threat exposed ecosystems and humans through food chain.

Based on the gathered and reviewed information of Tables 1 and 2 was created after the classification of each pesticide compound into 20 main chemical groups and one last group that was named “others” containing all the compounds that could not be classified to any of the previous 20 ones, such as aminomethylphosphonic acids, thiadiazines, triketones, uracils, nitriles, dicarboximides, anthranilic diamides; halogenated pyrroles; benzoylureas; pyridazinones; dimethoxybenzenes chloro substituted; isoxazolidinones; pyrazole carboxamides; disulfides; thiazole carboxamides; benzofuranyl alkylsulfonates; organobromines; thiadiazoles; phosphoramido compounds; phenylamides; dinitroanilines; isoxazoles; pyrimidines, phenols, etc.

As shown from the obtained information, it is obvious that the majority of the studies ( $\approx 18\%$ ) are dealing with the chemical group of organophosphorus pesticides and their transportation behavior in soils (Fig. 4). Afterward, the chemical groups of amide and acetamide herbicides and fungicides (with 12 totally studied chemical compounds), sulfonyleurea herbicides (among which the most studied compounds were sulfometuron-methyl with five reports and nicosulfuron with four reports) and conazole fungicides (among which the most surveyed molecules were tebuconazole with 12 reports and penconazole with four reports) are following in the

**Table 1** Reports reviewed in the current overview regarding the scientific published data on (ad)sorption/desorption and leaching of pesticides in natural soil matrices. The search was based on “Scopus Database” and only original research publications since 2016 are included. Reports are presented in alphabetical order of the pesticides’ name

No.	Pesticide name	Chemical group	Process studied	Reference(s)
1	Abamectin	Avermectin	(Ad)sorption/ desorption	[35, 36]
2	Acetamiprid	Neonicotinoid insecticides	Dissipation	[36]
3	Acetochlor	Anilide herbicides (Chloroacetanilides)	(Ad)sorption/ desorption	[37–39]
4	Alachlor	Anilide herbicides (Chloroacetanilides)	Vertical mobility	[39]
5	Ametryn	Triazine herbicides (Thiotriazines)	(Ad)sorption/ desorption	[40]
6	Aminocyclopyrachlor	Pyrimidine, cyclopropane and organochlorine pesticides	(Ad)sorption/ desorption	[41–45]
7	AMPA (Aminomethylphosphonic acid)	Aminomethylphosphonic acids	Leaching	[41, 45]
8	Atrazine (and transformation product: 2-hydroxyatrazine)	Triazine herbicides	Vertical transport	[24]
9	Azimsulfuron	Sulfonyleurea herbicides ( <i>N</i> -sulfonyleureas)	Leaching	[46]
			Leaching	[47, 48]
			Vertical mobility	[1]
			(Ad)sorption/ desorption	[34, 35, 49–66]
			Leaching	[46, 53, 66–68]
			Runoff in soil	[53]
			Vertical mobility	[24]
			Dissipation	[58]
			(Ad)sorption/ desorption	[69]

10	Azinphos-methyl	Organophosphorus insecticides	(Ad)sorption/ desorption	[28]
11	Azoxystrobin	Strobilurin fungicides (Aryloxyrimidines)	(Ad)sorption/desorption Desorption Leaching Vertical mobility	[70-72] [70] [72] [73]
12	Benomyl	Carbamate fungicides (Benzimidazoles)	(Ad)sorption/ desorption	[74, 75]
13	Bentazone	Other herbicides: Thiadiazines	(Ad)sorption/ desorption Leaching Dissipation Dissipation	[21] [76, 77] [29]
14	Benzobicyclon	Other herbicides: Carbobicyclics (chloro-substituted), Triketones	(Ad)sorption/ desorption	[78]
15	Bifenthrin	Pyrethroid insecticides	(Ad)sorption/ desorption	[79-81]
16	Bispyribac-sodium	Benzoic acid herbicides	Leaching Dissipation	[79-81] [79, 81]
17	Boscalid	Amide herbicides (Pyridinecarboxamide)	(Ad)sorption/ desorption Leaching Dissipation	[71, 75] [82, 83] [77] [84]
18	Bromacil	Uracil herbicides	Adsorption/desorption and vertical mobility	[85]
19	Bromoxynil	Nitrile herbicides (phenols)	Dissipation	[86]
20	Butachlor	Anilide herbicides (Acetanilides)	Dissipation	[86]

(continued)

Table 1 (continued)

No.	Pesticide name	Chemical group	Process studied	Reference(s)
21	Cadusafos	Organophosphorus insecticides	Adsorption/desorption	[87]
			Dissipation	[71, 88]
			Plant uptake	[88]
22	Captan	Dicarboximide fungicides (Phthalimides)	Adsorption/desorption	[89]
23	Carbaryl	Carbamate insecticides	Adsorption/desorption	[50, 90, 91]
			Leaching	[91]
24	Carbendazim	Carbamate fungicides	Adsorption/desorption	[92–94]
25	Carbofuran	Carbamate insecticides	Adsorption/desorption	[41, 90, 95–97]
			Leaching	[41]
			Vertical mobility	[24]
26	Chlorantraniliprole	Anthranilic diamides	Adsorption/desorption	[98]
27	Chlorfenapyr	Other pesticides: Halogenated pyrroles	Adsorption/desorption	[99]
28	Chlorfenvinphos	Organophosphorus insecticides	Adsorption/desorption	[28, 45, 100]
			Leaching	[45]
29	Chlorfluazuron	Chitin synthesis inhibitors and benzoylureas (insect growth regulators)	Adsorption/desorption	[101]
30	Chloridazon	Other herbicides: Pyridazinones	Leaching	[102]
31	Chloroneb	Other fungicides: Dimethoxybenzenes chloro substituted	Adsorption/desorption	[71]
32	Chlorotoluron	Phenylurea herbicides	Adsorption/desorption	[20, 23, 103–106]
33	Chlorothalonil	Organochlorine fungicides (Dinitriles)	Adsorption/desorption	[107–109]
			Leaching	[107]
34	Chlorpyrifos (and metabolite 3,5,6-trichloro-2-pyridinol)	Organophosphorus insecticides	Adsorption/desorption	[28, 45, 58, 89, 91, 100, 108–123]
			Leaching	[45, 91, 112, 117]

			Dissipation	[58, 121, 122]
35	Chlorpyrifos-methyl	Organophosphorus insecticides	Adsorption/desorption	[100]
36	Chlorsulfuron	Sulfonylurea herbicides	Adsorption/desorption	[124]
37	Clomazone	Other herbicides: Isoxazolidinones	Adsorption/desorption	[80, 124–126]
			Leaching	[83, 126]
			Dissipation	[126]
38	Cymoxanil	Acetamide	Adsorption/desorption	[127]
			Leaching	[128]
			Dissipation	[129]
39	Clothianidin	Neonicotinoid insecticides	Adsorption/desorption	[37, 71, 130–136]
			Plant uptake	[131]
40	Croxyphos	Organophosphorus insecticides	Adsorption/desorption	[28]
41	Cyantraniliprole	Pyrazole carboxamides insecticides	Adsorption/desorption	[137]
42	Cypermethrin	Pyrethroid insecticides	Adsorption/desorption	[89, 99, 138]
43	2-Chlorophenol	Organochlorine insecticides, phenols	Adsorption/desorption	[139]
44	DDT (dichlorodiphenyltrichloroethane)	Organochlorine insecticides	Adsorption/desorption	[140, 141]
45	Deltamethrin	Pyrethroid insecticides	Adsorption/desorption	[138]
46	Demeton	Organophosphorus insecticides	Adsorption/desorption	[28]
47	Diazinon	Organophosphorus insecticides	Adsorption/desorption	[28, 71, 108, 110, 142]
48	Dichlorvos	Organophosphorus insecticides	Adsorption/desorption	[28, 115]
49	Diclocymet	Amide fungicides	Adsorption/desorption	[71]
50	Dicofol	Organochlorine acaricides	Adsorption/desorption	[89]
51	Dicrotophos	Organophosphorus insecticides	Adsorption/desorption	[28]
52	Difenoconazole	Conazole fungicides	Adsorption/desorption, and plant uptake	[143]
53	Diflufenican	Pyridine herbicides (pyridine carboxamides)	Adsorption/desorption	[144]
			Leaching	[83]
			Dissipation	[76]

(continued)

Table 1 (continued)

No.	Pesticide name	Chemical group	Process studied	Reference(s)
54	Dimethenamid	Amide herbicides (Chloroacetamides)	Adsorption/desorption Dissipation	[138, 145, 146] [145]
55	Dimethoate	Organophosphorus insecticides	Adsorption/desorption	[28, 71, 114, 142]
56	Dinotefuran	Neonicotinoid insecticides	Adsorption/desorption	[71, 134]
57	Disulfoton	Organophosphorus insecticides	Adsorption/desorption	[28]
58	Diuron	Phenylurea herbicides	Adsorption/desorption Leaching Dissipation Vertical mobility	[20, 84, 103, 147–159] [67, 117, 159–161] [145] [24, 84]
59	2,4-D (2,4-Dichlorophenoxyacetic acid)	Phenoxy herbicides	Adsorption/desorption Dissipation Diffusion Vertical mobility	[34, 90, 150, 162–166] [85] [164] [166]
60	2,4-DB (4-(2,4-Dichlorophenoxy) butyric acid)	Phenoxy herbicides	Adsorption/desorption	[56]
61	2,4-Dichlorophenol	Organochlorine insecticides, phenols	Adsorption/desorption	[139]
62	DMDS (Dimethyldisulfide)	Disulfides	Adsorption/desorption	[167]
63	2,6-Dimethylphenol	Phenols	Adsorption/desorption	[139]
64	Endosulfan	Organochlorine insecticides	Adsorption/desorption Dissipation	[121, 123, 168] [121]
65	Epoxiconazole	Conazole fungicides	Adsorption/desorption Dissipation	[58, 169] [58, 76]
66	Ethaboxam	Thiazole carboxamide fungicides	Adsorption/desorption	[170]
67	Ethion	Organophosphorus insecticides	Adsorption/desorption	[28, 89]
68	Ethiprole	Pyrazole insecticides (Phenylpyrazoles)	Adsorption/desorption	[71]

69	Ethofumesate	Other herbicides: Benzofuranyl alkylsulfonates	Adsorption/desorption, and leaching	[26]
70	Ethoprophos	Organophosphorus insecticides	Adsorption/desorption, and leaching	[41]
71	Ethylene dibromide	Organobromines	Leaching	[68]
72	Etridiazole	Thiadiazole fungicides	Adsorption/desorption, and leaching	[41]
73	Fenamiphos	Phosphoramido insecticides	Adsorption/desorption	[88, 171]
			Vertical mobility	[171]
			Dissipation	[88]
74	Fenarimol	Pyrimidine fungicides	Adsorption/desorption	[138, 146]
75	Fenchlorphos	Organophosphorus insecticides	Adsorption/desorption	[28]
76	Fenitrothion	Organophosphorus insecticides	Adsorption/desorption	[28, 71]
77	Fenobucarb	Carbamate insecticides	Adsorption/desorption	[71, 134]
78	Fenthion	Organophosphorus insecticides	Adsorption/desorption	[28, 71, 126]
79	Fipronil (and degradation products: fipronil desulfanyl, fipronil sulfone, fipronil sulfide)	Pyrazole insecticides (Phenylpyrazoles)	Adsorption/desorption	[49, 65, 71, 172]
80	Flonicamid	Other insecticides: Pyridines	Leaching	[82]
81	Fluazifop	Phenoxy herbicides (Aryloxy-phenoxypropionates)	Adsorption/desorption	[173]
82	Flucetosulfuron	Sulfonyleurea herbicides	Adsorption/desorption, and leaching	[174]
83	Fludioxonil	Other fungicides: Phenylpyrroles	Adsorption/desorption, and leaching	[70]
84	Flufenacet	Anilide herbicides (Oxyacetanilides)	Adsorption/desorption	[23, 104, 106]
85	Flumetsulam	Anilide herbicides (Triazolopyrimidines)	Adsorption/desorption	[163]
86	Flumioxazin	N-phenylphthalimide herbicides	Adsorption/desorption	[50]
87	Flusilazole	Conazole fungicides	Adsorption/desorption	[58, 175]

(continued)

Table 1 (continued)

No.	Pesticide name	Chemical group	Process studied	Reference(s)
			Leaching	[175]
			Dissipation	[58]
88	Fosthiazate	Organophosphorus nematocides	Adsorption/desorption	[71, 131, 134, 176]
			Plant uptake	[131]
89	Flutolanil	Amide fungicides (Benzamides)	Adsorption/desorption	[71, 131, 134]
			Plant uptake	[131]
90	Fluxapyroxad	Pyrazolecarboxamide (anilide) fungicides	Adsorption/desorption	[177]
91	Glyphosate	Organophosphorus herbicides	Adsorption/desorption	[51, 152, 154, 157, 178–182]
			Leaching	[68, 117, 178]
			Dissipation	[76]
			Vertical mobility	[1]
92	Hexazinone	Triazinone herbicides	Adsorption/desorption	[50, 147, 149, 151, 153, 183–186]
			Leaching	[68, 160, 161, 185, 186]
93	Hexaconazole	Conazole fungicides	Adsorption/desorption	[105, 187]
94	Indaziflam	Alkylazine herbicides (Fluoroalkyltriazines)	Adsorption/desorption	[188]
95	Imazamox	Imidazolinone herbicides	Adsorption/desorption	[189]
96	Imazapic	Imidazolinone herbicides	Adsorption/desorption	[190]
97	Imazapyr	Imidazolinone herbicides	Adsorption/desorption	[190]
98	Imazaquin (S- and R- enantiomers)	Imidazolinone herbicides	Adsorption/desorption	[191, 192]
			Leaching	[191]
			Dissipation	[191]
99	Imidacloprid	Neonicotinoid insecticides	Adsorption/desorption	[47, 50, 63, 71, 131, 134–136, 163–196]
			Leaching	[21, 47, 193, 195, 196]
			Dissipation	[76]
			Plant uptake	[131]



100	Iodosulfuron	Sulfonylurea herbicides	Adsorption/desorption	[197]
101	Iprodione	Dicarboximide fungicides	Adsorption/desorption	[93]
102	Isoproturon	Phenylurea herbicides	Adsorption/desorption	[20, 31, 63, 66, 103, 125, 154, 197–199]
			Leaching	[66]
			Dissipation	[122]
103	Kresoxim-methyl	Strobilurin fungicides	Adsorption/desorption	[71, 72]
			Vertical mobility	[72]
104	Lambda-cyhalothrin	Pyrethroid insecticides	Adsorption/desorption	[200]
105	Linuron	Phenylurea herbicides	Adsorption/desorption	[20, 44, 103]
106	MCPA (2-methyl-4-chlorophenoxyacetic acid)	Phenoxy herbicides	Adsorption/desorption	[50, 90]
			Leaching	[76, 83, 117]
107	Na-K-DMA MCPA salt (dimethyl ammonium-potassium-sodium salt of (4-chloro-2-methylphenoxy) acetic acid)	Phenoxy herbicides	Adsorption/desorption	[201]
108	Malathion	Organophosphorus insecticides	Adsorption/desorption	[28]
109	Metalddehyde	Other pesticides: Molluscicides, Tetraoxacyclootanes	Leaching	[202]
110	Mesotrione	Benzoylcyclohexane-1,3-dione herbicides	Adsorption/desorption	[203]
			Leaching	[202]
			Dissipation	[204]
111	Metalaxyl (R-, and S-enantiomers)	Phenylamides (acylalanines)	Adsorption/desorption	[44, 70, 71, 131, 134, 176, 205–210]
			Leaching	[70, 205, 209, 210]
			Dissipation	[207, 210]
			Plant take-up	[131]
112	Metazachlor	Pyrazole herbicides	Leaching	[68]
			Dissipation	[76]

(continued)

Table 1 (continued)

No.	Pesticide name	Chemical group	Process studied	Reference(s)
113	Methidathion	Organophosphorus insecticides	Adsorption/desorption	[71]
114	Metolachlor (and its oxanilic and ethane sulfonic acids metabolites)	Anilide herbicides (Chloroacetamides)	Adsorption/desorption	[25, 33, 47, 61, 90, 154, 203, 211–215]
			Leaching	[25, 33, 47, 215]
			Dissipation	[86, 215]
			Transport behavior	[212]
115	Metsulfuron-methyl	Sulfonylurea herbicides	Adsorption/desorption	[50]
			Dissipation	[85]
116	Metribuzin	Triazinone herbicides	Adsorption/desorption	[185]
			Leaching	[102, 185]
117	Mevinphos	Organophosphorus insecticides	Adsorption/desorption	[28]
118	Monocrotophos	Organophosphorus insecticides	Adsorption/desorption	[28]
119	Monuron	Phenylurea herbicides	Adsorption/desorption	[20, 103]
120	Myclobutani	Conazole fungicides	Leaching	[82]
121	Napropamide	Amide herbicides	Adsorption/desorption, and leaching	[41]
122	Nicosulfuron	Sulfonylurea herbicides	Adsorption/desorption	[216–218]
			Leaching	[202]
123	Nonylphenols mixture	Nonylphenol	Adsorption/desorption	[219]
124	2-Nitrophenol	Nitrophenol herbicides	Adsorption/desorption	[139]
125	Oxadixyl	Amide fungicides	Adsorption/desorption	[97]
126	Oxyfluorfen	Diphenyl ether herbicides	Adsorption/desorption	[176]
127	Paichongding	Neonicotinoid insecticides (cis-nitromethylene neonicotinoids)	Adsorption/desorption, and leaching	[220]
128	Parathion	Organophosphorus insecticides	Adsorption/desorption	[28, 123]
129	Parathion methyl	Organophosphorus insecticides	Adsorption/desorption	[28, 89, 123, 142]

130	Penconazole	Conazole fungicides	Adsorption/desorption Leaching	[22, 175, 221] [82, 175, 221]
131	Pendimethalin	Dinitroamine herbicides	Adsorption/desorption	[58, 138, 145, 176, 222, 223]
132	Penflufen	Organofluorine aromatic amide fungicides, Pyrazole carboximides	Dissipation Adsorption/desorption	[58, 145] [177]
133	Penoxsulam	Amide herbicides	Adsorption/desorption	[69]
134	Pentachlorophenol	Organochlorines, phenols	Adsorption/desorption Leaching	[224–226] [227]
135	Permethrin	Pyrethroid insecticides	Adsorption/desorption	[123]
136	Pethoxamid	Amide herbicides (Chloroacetamides)	Dissipation	[204]
137	Phenamacril	Strobilurin fungicide (cyanoacrylate)	Adsorption/desorption, and vertical mobility	[72]
138	Phenthoate	Organophosphorus insecticides	Adsorption/desorption	[28]
139	Phorate	Organophosphorus insecticides	Adsorption/desorption	[28]
140	Phosmet	Organophosphorus insecticides	Adsorption/desorption	[28]
141	Picloram	Pyridine herbicides	Adsorption/desorption Leaching	[189] [68]
142	Pirimicarb	Carbamate insecticides	Adsorption/desorption	[123, 127]
143	Pirimiphos ethyl	Organophosphorus insecticides	Adsorption/desorption	[123]
144	Prochloraz	Amide fungicides (Imidazoles)	Adsorption/desorption Dissipation	[58, 123] [58]
145	Procymidone	Dicarboximide fungicides	Adsorption/desorption Leaching	[71, 131, 134] [131]
146	Prometryn	Triazine herbicides (Diamino-1,3,5-triazines)	Adsorption/desorption	[105, 123]
147	Propanil	Anilide herbicides (Acetanilides)	Vertical mobility	[24]
148	Propiconazole	Conazole fungicides	Adsorption/desorption	[27, 71]

(continued)

**Table 1** (continued)

No.	Pesticide name	Chemical group	Process studied	Reference(s)
			Leaching	[83]
149	Propyzamide	Amide herbicides (Benzamides)	Adsorption/desorption and leaching	[228]
150	Prosulfocarb	Thiocarbamate herbicide	Adsorption/desorption	[106]
			Leaching	[229]
			Dissipation	[230]
151	Pymetrozine	1,2,4-Triazine antifeedants (insect growth regulators)	Adsorption/desorption	[231]
152	Pyrasulfotole	Isoxazole herbicides	Dissipation	[85]
153	Pyrimethanil	Pyrimidine fungicides (Aminopyrimidines)	Adsorption/desorption	[75]
			Dissipation	[77]
154	Quinclorac	Benzoic acid herbicides (Quinolines carboxylic acids)	Adsorption/desorption	[223]
155	Quinoxifen	Other fungicides	Adsorption/desorption	[122]
156	Quizalofop-P-ethyl	Phenoxy herbicides (Aryloxyphenoxypropionic acids)	Adsorption/desorption	[157]
157	Sedaxane	Pyrazole-4-carboxylic acid amide fungicides (Organofluorines and pyrazole carboxamides)	Adsorption/desorption and leaching	[70]
158	Siduron	Phenylurea herbicides	Adsorption/desorption and leaching	[232]
159	Simazine	Triazine herbicides	Leaching	[233]
			Adsorption/desorption	[234, 235]
160	Sulfentrazone	Substituted triazole herbicides	Adsorption/desorption	[163, 178]
			Leaching	[178]
161	Sulfometuron-methyl	Sulfonylurea herbicides	Adsorption/desorption	[147, 149, 236]
			Leaching	[160, 161]

162	Sulfofep	Organophosphorus insecticides	Adsorption/desorption and leaching	[142]
163	Tebuconazole	Conazole fungicides	Adsorption/desorption	[41, 58, 122, 127, 131, 169, 179, 207, 237, 238]
			Leaching	[41, 128]
			Dissipation	[58, 125, 129, 207]
			Plant take-up	[131]
164	Tebuthiuron	Urea herbicides (Dimethylureas)	Adsorption/desorption	[183, 186]
			Leaching	[186]
165	Terbufos	Organophosphorus insecticides	Adsorption/desorption	[28]
166	Terbutylazine	Triazine herbicides (Chlorotriazines)	Adsorption/desorption	[50, 173, 189, 203]
			Dissipation	[76]
167	Terbutryn	Triazine herbicides	Adsorption/desorption and leaching	[26]
168	Tetraconazole	Conazole fungicides	Adsorption/desorption	[71]
169	Tetradifon	Tetrachlorodiphenyl sulfone acaricides	Adsorption/desorption	[71]
170	Thiabendazole	Thioazole fungicides (Benzimidazoles)	Adsorption/desorption and leaching	[70]
171	Thiacloprid	Neonicotinoid insecticides	Adsorption/desorption	[37, 71, 131, 134–136, 138, 238–241]
			Leaching	[239]
			Uptake	[131]
172	Thiamethoxam	Neonicotinoid insecticides	Adsorption/desorption	[37, 70, 133, 242]
			Leaching	[70, 196]
			Dissipation	[242]
			Uptake	[242]
173	Thiencarbazone-methyl	<i>N</i> -sulfonylurea herbicides (sulfonyl-amino-carbonyl-triazolinones)	Dissipation	[85]

(continued)

Table 1 (continued)

No.	Pesticide name	Chemical group	Process studied	Reference(s)
174	Thifensulfuron-methyl	Sulfonylurea herbicides	Dissipation	[85]
175	Thiram	Dithiocarbamate fungicides	Adsorption/desorption	[243]
176	Thymol	Phenols	Adsorption/desorption	[244]
177	Tolclofos-methyl	Organophosphorus fungicides	Adsorption/desorption	[71, 134]
178	Triadimefon	Conazole fungicides	Adsorption/desorption	[123]
179	Triadimenol	Triazoles	Adsorption/desorption	[127]
180	Triasulfuron	Sulfonylurea herbicides (N-sulfonylureas)	Adsorption/desorption	[106, 245, 246]
181	Tribenuron-methyl	Sulfonylurea herbicides	Dissipation	[204]
182	Trichlorfon (or Metrifonate)	Sulfonylurea herbicides	Dissipation	[85]
183	Triclosan	Organophosphorus insecticides	Adsorption/desorption	[28]
184	Triclopyr	Polychloro phenoxy phenols	Adsorption/desorption	[156]
185	Trifloxystrobin	Pyridine herbicides	Adsorption/desorption	[173]
186	Triflumezopyrim	Strobilurin fungicides	Adsorption/desorption	[71]
		Pyridopyrimidinone insecticides	Adsorption/desorption	[247]

**Table 2** Classification of reports reviewed in the current overview regarding the recently published scientific published data on (ad)sorption/desorption and leaching of pesticides in natural soil matrices. The search was based on “Scopus Database” and only original research publications since 2016 are included

	Chemical groups	No. of target pesticides	Pesticide compounds (number of found and reviewed data)
1	Amide and acetamide herbicides, and fungicides	12	Boscalid (5); Cymoxanil (3); Diclocymet (1); Dimethenamid (3); Flutolanil (3); Napropamide (1); Oxadixyl (1); Penflufen (1); Penoxsulam (1); Pethoxamid (1); Prochloraz (2); Propyzamide (1)
2	Anilide herbicides, and fungicides	8	Acetochlor (1); Alachlor (5); Butachlor (2); Flufenacet (3); Flumetsulam (1); Fluxapyroxad (1); Metolachlor (13); Propanil (1)
3	Benzoic acid herbicides	2	Bispyribac-sodium (3); Quinclorac (1)
4	Carbamate, thiocarbamate, and dithiocarbamate insecticides, herbicides, and fungicides	8	Benomyl (1); Carbaryl (3); Carbendazim (3); Carbofuran (6); Fenobucarb (2); Pirimicarb (2); Prosulfocarb (3); Thiram (1)
5	Conazole fungicides	10	Difenoconazole (1); Epoxiconazole (3); Flusilazole (2); Hexaconazole (2); Myclobutanil (1); Penconazole (4); Propiconazole (3); Tebuconazole (12); Tetraconazole (1); Triadimefon (1)
6	Diphenyl ether herbicides	1	Oxyfluorfen (1)
7	Imidazolinone herbicides	4	Imazamox (1); Imazapic (1); Imazapyr (1); Imazaquin (2)
8	Neonicotinoid insecticides	7	Acetamiprid (3); Clothianidin (9); Dinotefuran (2); Imidacloprid (15); Paichongding (1); Thiacloprid (10); Thiamethoxam (5)
9	Organochlorine insecticides, fungicides, and acaricides	8	Aminocyclopyrachlor (2); Chlorothaliniol (3); 2-Chlorophenol (1); DDT (2); Dicofol (1), 2,4-Dichlorophenol (1); Endosulfan (3); Pentachlorophenol (4)
10	Organophosphorus insecticides, herbicides, fungicides, and nematocides	33	Azinphos-methyl (1); Cadusafos (2); Chlorfenvinphos (3); Chlorpyrifos (21); Chlorpyrifos-methyl (1); Crotoxyphos (1); Demeton (1); Diazinon (5); Dichlorvos (2); Dicrotophos (1); Dimethoate (4); Disulfoton (1); Ethion (2); Ethoprophos (1); Fenchlorphos (1); Fenitrothion (2); Fenthion (3); Fosthiazate (4); Glyphosate (13) Malathion (1); Methidathion (1); Mevinphos (1);

(continued)

**Table 2** (continued)

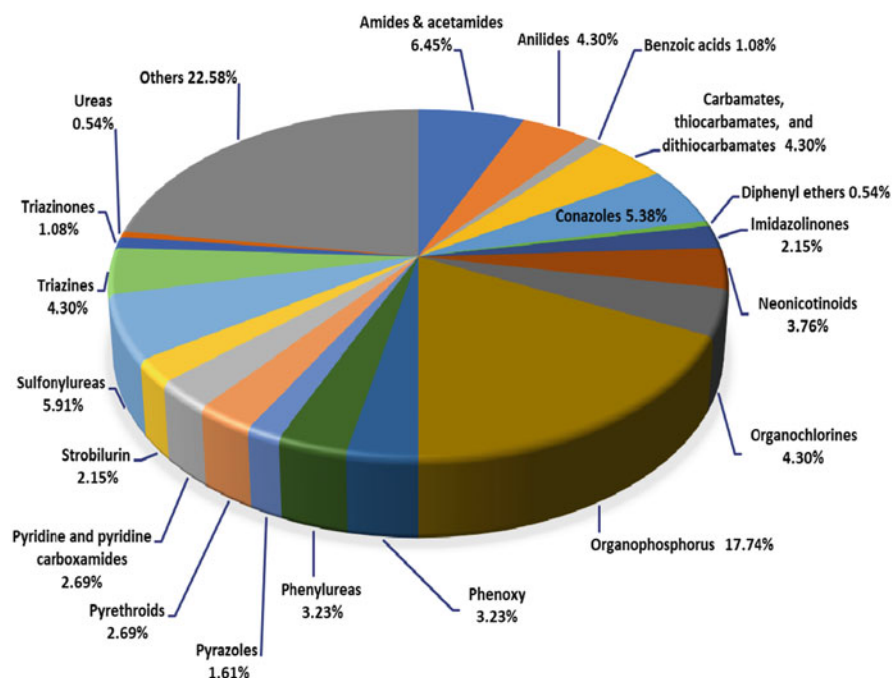
	Chemical groups	No. of target pesticides	Pesticide compounds (number of found and reviewed data)
			Monocrotophos (1); Parathion (2); Parathion methyl (4); Phenthoate (1); Phorate (1); Phosmet (1); Pirimiphos-ethyl (1); Sulfotep (1); Terbufos (1); Trichlorfon (or Metrifonate) (1); Toclufos-methyl (1)
11	Phenoxy herbicides	6	2,4-D (9); 2,4-dB (1); Fluazifop (1); MCPA (5); Na-K-DMA MCPA salt (1); Quizalofop-P-ethyl (1)
12	Phenylurea herbicides	6	Chlorotoluron (6); Diuron (21); Isoproturon (9); Linuron (3); Monuron (2); Siduron (1)
13	Pyrazole	3	Ethiprole (1); Fipronil (4); Metazachlor (2)
14	Pyrethroid insecticides	5	Bifenthrin (1); Cypermethrin (3); Deltamethrin (1); Lambda-cyhalothrin (1); Permethrin (1)
15	Pyridine and pyridine carboxamides insecticides and herbicides	5	Boscalid (5); Diflufenican (3); Flonicamid (1); Picloram (2); Triclopyr (1)
16	Strobilurin fungicides	4	Azoxystrobin (3); Kresoxim-methyl (2); Phenamacril (1); Trifloxystrobin (1)
17	Sulfonylurea herbicides	11	Azimsulfuron (1); Chlorsulfuron (1); Flucetosulfuron (1); Iodosulfuron (1); Metsulfuron-methyl (2); Nicosulfuron (4); Sulfometuron-methyl (5); Thiencarbazone-methyl (1); Thifensulfuron-methyl (1); Triasulfuron (4); Tribenuron-methyl (1)
18	Triazine herbicides	8	Ametryn (2); Atrazine (24); Indaziflam (1); Prometryn (2); Pymetrozine (1); Simazine (4); Terbutylazine (5); Terbutryn (1)
19	Triazinone herbicides	2	Hexazinone (12); Metribuzin (2)
20	Urea herbicides	1	Tebuthiuron (2)
21	Others: Aminomethylphosphonic acids, Thiadiazines, Triketones, Uracils, Nitriles, Dicarboximides, Anthranilic diamides; Halogenated pyrroles; Benzoylureas; Pyridazinones; Dimethoxybenzenes chloro substituted; Isoxazolidinones; Pyrazole carboxamides; Disulfides; Thiazole Carboxamides; Benzofuranyl alkylsulfonates; Organobromines; Thiadiazoles; Phosphoramido	42	Abamectin (2); AMPA (1); Bentazone (5); Benzobicyclon (1); Bromacil (1); Bromoxynil (1); Captan (1); Chlorantraniliprole (1); Chlorfenapyr (1); Chlorfluazuron (1); Chloridazon (1); Chloroneb (1); Clomazone (4); Cyantraniliprole (1); DMDS (1); Ethaboxam (1); Ethofumesate (1); Ethylene dibromide (1); Etridiazole (1); Fenamiphos (2); Fenarimol (2); Fludioxonil (1); Flumioxazin (1);

(continued)



**Table 2** (continued)

Chemical groups	No. of target pesticides	Pesticide compounds (number of found and reviewed data)
compounds; Phenylamides; Dinitroanilines; Isoxazoles; Pyrimidines, Phenols, etc.		Iprodione (1); Metaldehyde (1); Mesotrione (3); Metalaxyl (12); 2-Nitrophenol (1), Nonylphenol (1); Pendimethalin (6); Procymidone (3); Pyrasulfotole (1); Pyrimethanil (2); Quinoxifen (1); Sedaxane (1); Sulfentrazone (2); Tetradifon (1); Thiabendazole (1); Thymol (1); Triadimenol (1); Triclosan (1); Triflumezopyrim (1)



**Fig. 4** Overall relative frequency of reports for different chemical groups of pesticides concerning their (ad)sorption/desorption and leaching phenomena in natural soil matrices overviewed in present review. The search was based on “Scopus Database” using as keywords the terms pesticide, soil, and sorption or desorption or leaching; only original research publications since 2016 were considered, while all critical reviews and overviews published in the same period were excluded. Target pollutants are tested either individually or in mixture with other toxic chemicals

second, third, and fourth place by scoring almost 6.5%, 6%, and 5.5% of relative literature found, respectively.

In Table 3 detailed information is presented regarding the recently published scientific published data on the performed experimental procedures for the assessment of some selected pesticides' transportation capacity and the main findings of some selected reviewed articles. According to the reviewed records addressed in this overview most studies employed and applied the OECD 106 guideline of batch equilibrium method for adsorption-desorption proposed by the Organization for Economic Co-operation and Development (OECD) [248] while the use of soil columns is also an alternative method preferred in a lower number of published research.

Furthermore, from the selected data that are presented in Table 3 it is obvious that there is a great variation between the estimated adsorption and desorption coefficient values of pesticides depended not only on the physicochemical properties of the tested soils but also on the characteristics of the pesticides. This observation is in accordance with other data published previously in research and review studies which highlighted the fact that besides the various sorption parameters which can be observed and measured for the same pesticide in different soil matrices, also a variability among different pesticide compounds adsorbed on the same soil matrix can exist [8, 14, 18, 145]. In the study of Zhang et al. [135] who investigated the sorption, desorption, and degradation kinetics of three neonicotinoid insecticides in four agricultural soils of different texture (two loam and two clay loam type) and different physicochemical properties such as cation exchange capacity (CEC), OM content, and pH a wide variety of sorption and desorption parameters were reported. For instance, the values of Freundlich equilibrium constant  $K_F$  (in  $(\text{mg}/\text{kg})(\text{mg}/\text{L})^{-n}$ ) for clothianidin were calculated between the range of 0.992 and 3.39, whereas the same parameter of sorption affinity for the other two selected neonicotinoids imidacloprid and thiacloprid varied between 1.01–3.42 and 1.16–9.06, correspondingly. Low sorption of all three neonicotinoids was generally observed that was mainly affected by the SOM content following the order thiacloprid > imidacloprid  $\approx$  clothianidin [135].

Many of the reported data were explained by the phenomenon of hysteresis in soil (ad)sorptive and/or desorptive processes. Based on our observation sorption-desorption hysteresis phenomena have been reported in several overviewed bibliographies influencing and controlling the distribution of pesticides into soil-water-biota systems [57, 60, 125, 173, 174, 199]. As reported in the literature, the effect of desorption hysteresis may be observed when the desorption of adsorbed pesticide molecules is not allowed to occur immediately due to the high-strength chemical bonds that were developed in the sorption process [57, 60, 125, 173, 174, 199]. Usually, hysteresis is quantified in terms of the extra Gibbs free energies of high-energy sorption sites that are sorbate- and sorbent-dependent, varying across sorption isotherms [125]. In the recently published study of Đurović-Pejčev et al. [125] regarding the adsorption-desorption behavior of clomazone in two Serbian agricultural the hysteresis effect that was observed in both tested soils increased with the increase of clomazone's initial concentration in the soil-water system, whereas the percentage of desorbed amount during successive desorption cycles decreased. On the contrary,

**Table 3** Detailed information contained in selected scientific reports reviewed within the current overview regarding the published data on (ad)sorption/desorption and leaching of pesticides in natural soil matrices. The illustrated research results were retrieved by “Scopus Database” by using as keywords the terms pesticide, soil, and sorption or desorption or leaching. Target PPP pollutants were tested either individually or in mixture with other toxic substances. Only original research publications since 2016 are included, whereas critical reviews and overviews published in the same period were excluded

Pesticide name (chemical class)	Soil content and physicochemical properties										Experimental method/ Isotherm model		Estimated parameters		Reference
	Type (texture)	% Sand	% Silt	% Clay	CEC (cmol kg <sup>-1</sup> )	% OC	pH	Other information available	Batch equilibrium/ Freundlich	Sorption process	Desorption process				
Acetamiprid (neonicotinoid)	Arable soil (clay loam)	54.4	20.8	24.8	20.4	3.43	5.9 (in water)	%HAs = 1.72; % FAs = 0.22 Major soil minerals: Kaolinite, vermiculite-chlorite intermediate structures, and Illite. Minerals (g kg <sup>-1</sup> ): Al <sub>pyz</sub> = 5.1 <sup>a</sup> , Fe <sub>pyz</sub> = 0.62 <sup>a</sup> , Al <sub>ox</sub> = 13 <sup>b</sup> , Fe <sub>ox</sub> = 6.7 <sup>b</sup> , Si <sub>ox</sub> = 1.0 <sup>b</sup> , Al <sub>DCH</sub> = 1.1 <sup>c</sup> , Fe <sub>DCH</sub> = 6.9 <sup>c</sup>	Batch equilibrium/ Freundlich	$K_F = 8.580$ $1/n_F = 0.8910$ $R^2 = 0.9896$		[38]			
Bromacil (substituted uracil)	Agricultural soil	13	10	77		2.03	4.2		Batch equilibrium/ Freundlich	$K_F = 0.37$ $1/n_F = 0.64$ $K_{oc} = 18.43$		[84]			
Chlorpyrifos (organophosphate)	Field soil (sandy loam)	89.5	6.8	3.7		1.52	7.53 (in water)	Total N (g kg <sup>-1</sup> ) = 0.44; P <sub>2</sub> O <sub>5</sub> (g kg <sup>-1</sup> ) = 0.02; K <sub>2</sub> O (g kg <sup>-1</sup> ) = 0.043 Soil microbial biomass carbon (mg C kg <sup>-1</sup> ) = 160.2	Batch equilibrium/ Freundlich	Active ingredient: $K_F = 195.2$ $n_F = 0.700$ $R^2 = 0.988$ $K_{oc} = 12,842.6$ Commercial formulation: $K_F = 211.4$ $n_F = 0.501$ $R^2 = 0.987$ $K_{oc} = 13,906.9$		[122]			

(continued)

Table 3 (continued)

Pesticide name (chemical class)	Soil content and physicochemical properties							Other information available	Experimental method/ Isotherm model	Estimated parameters		Reference
	Type (texture)	% Sand	% Silt	% Clay	CEC ( $\text{cmol kg}^{-1}$ )	% OC	pH			Sorption process	Desorption process	
Clothianidin (neonicotinoid)	Black soil (loam)	52	42	6	61.3	3.08	7.2 (in $\text{CaCl}_2$ )	Available nutrients ( $\text{mg kg}^{-1}$ ): $N = 279$ , $P = 52.2$ ; electrical conductivity ( $\text{dS m}^{-1}$ ) <sup>d</sup> = 524	Batch equi- librium/ Freundlich	$K_F = 3.39$ $n_F = 0.853$ $R^2 = 0.986$	$K_F = 5.05$ $n_F = 0.723$ $R^2 = 0.971$	[135]
	Fluvo-aquic soil (loam)	49	42	9	18.3	1.26	4.9 (in $\text{CaCl}_2$ )	Available nutrients ( $\text{mg kg}^{-1}$ ): $N = 158$ , $P = 29.6$ ; electrical conductivity ( $\text{dS m}^{-1}$ ) <sup>d</sup> = 80.1		$K_F = 1.08$ $n_F = 0.991$ $R^2 = 0.996$	$K_F = 1.86$ $n_F = 0.977$ $R^2 = 0.982$	
	Paddy soil (clay loam)	32	46	22	14.2	1.43	4.4 (in $\text{CaCl}_2$ )	Available nutrients ( $\text{mg kg}^{-1}$ ): $N = 115$ , $P = 22.7$ ; electrical conductivity ( $\text{dS m}^{-1}$ ) <sup>d</sup> = 34.1		$K_F = 2.75$ $n_F = 0.779$ $R^2 = 0.956$	$K_F = 4.04$ $n_F = 0.594$ $R^2 = 0.951$	
Red soil (clay loam)	48	34	18	11.9	0.110	3.8 (in $\text{CaCl}_2$ )	Available nutrients ( $\text{mg kg}^{-1}$ ): $N = 33.8$ , $P = 2.10$ ; electrical conductivity ( $\text{dS m}^{-1}$ ) <sup>d</sup> = 157		$K_F = 0.992$ $n_F = 0.998$ $R^2 = 0.975$	$K_F = 1.32$ $n_F = 0.921$ $R^2 = 0.976$		
Vegetable garden soil (silt loam) Depth frac- tions: • 0- 130 mm • 130- 250 mm			19.3 23.3 18.3	10.9 (0- 130 mm) 11.9 (130- 250 mm) 12.1 (250- 400 mm)	0.31 0.14 0.08	6.85 (0- 130 mm) 6.96 (130- 250 mm) 5.65 (250- 400 mm)		Batch equi- librium/ Henry's linear	(0-130 mm): $K_d = 1.40$ ; $R^2 = 0.99$ ; $K_{oc} = 451$ (130-250 mm): $K_d = 1.21$ $R^2 = 0.99$ ; $K_{oc} = 864$ (250-400 mm): $K_d = 0.62$	(0-130 mm): $K_d = 0.53$ ; $R^2 = 0.92$ (130- 250 mm): $K_d = 1.05$ $R^2 = 0.99$ (250- 400 mm): $K_d = 0.62$	[133]	

	<ul style="list-style-type: none"> <li>• 250–400 mm</li> </ul>										$R^2 = 0.99$ ; $K_{oc} = 775$	$K_d = 0.52$ $R^2 = 0.98$
	Farm soil (fine sandy loam) Depth fractions: <ul style="list-style-type: none"> <li>• 0–130 mm</li> <li>• 130–250 mm</li> <li>• 250–400 mm</li> </ul>	17.0	18.9	0.30	6.08	0–130 mm): $K_d = 1.45$ ; $R^2 = 0.99$ ; $K_{oc} = 483$	(0–130 mm): $K_d = 0.79$ ; $R^2 = 0.99$	(130–250 mm): $K_d = 0.74$ $R^2 = 0.99$	(250–400 mm): $K_d = 0.82$ $R^2 = 0.99$	(0–130 mm): $K_d = 0.30$ ; $R^2 = 0.83$	(130–250 mm): $K_d = 0.23$ $R^2 = 0.94$	(250–400 mm): $K_d = 0.50$ $R^2 = 0.96$
	Farm soil (fine sandy loam) Depth fractions: <ul style="list-style-type: none"> <li>• 0–130 mm</li> <li>• 130–250 mm</li> <li>• 250–400 mm</li> </ul>	14.5	20.3	0.64	7.72	(0–130 mm): $K_d = 1.94$ $R^2 = 0.99$ ; $K_{oc} = 303$	(130–250 mm): $K_d = 1.62$ $R^2 = 0.99$ ; $K_{oc} = 405$	(250–400 mm): $K_d = 1.48$ $R^2 = 0.99$ ; $K_{oc} = 400$	(0–130 mm): $K_d = 0.30$ ; $R^2 = 0.83$	(130–250 mm): $K_d = 0.23$ $R^2 = 0.94$	(250–400 mm): $K_d = 0.50$ $R^2 = 0.96$	
Diuron (Dimethylurea)	Agricultural soil	77		2.03	4.2		Batch equilibrium/ Freundlich					[84]
Imidacloprid (neonicotinoid)	Black soil (loam)	6	61.3	3.08	7.2 (in CaCl <sub>2</sub> )	Available nutrients (mg kg <sup>-1</sup> ): N = 279, P = 52.2; electrical	Batch equilibrium/ Freundlich					[135]

(continued)

Table 3 (continued)

Pesticide name (chemical class)	Soil content and physicochemical properties						Experimental method/ Isotherm model	Estimated parameters		Reference	
	Type (texture)	% Sand	% Silt	% Clay	CEC ( $\text{cmol kg}^{-1}$ )	% OC		pH	Other information available		Sorption process
	Fluvo-aquic soil (loam)	49	42	9	18.3	1.26	4.9 (in $\text{CaCl}_2$ )	conductivity ( $\text{dS m}^{-1}$ ) $^d = 524$ Available nutrients ( $\text{mg kg}^{-1}$ ): $N = 158$ , $P = 29.6$ ; electrical conductivity ( $\text{dS m}^{-1}$ ) $^d = 80.1$	$K_F = 2.36$ $n_F = 0.987$ $R^2 = 0.953$	$K_F = 3.27$ $n_F = 0.919$ $R^2 = 0.953$	
	Paddy soil (clay loam)	32	46	22	14.2	1.43	4.4 (in $\text{CaCl}_2$ )	Available nutrients ( $\text{mg kg}^{-1}$ ): $N = 115$ , $P = 22.7$ ; electrical conductivity ( $\text{dS m}^{-1}$ ) $^d = 34.1$	$K_F = 2.62$ $n_F = 0.805$ $R^2 = 0.969$	$K_F = 3.50$ $n_F = 0.650$ $R^2 = 0.963$	
	Red soil (clay loam)	48	34	18	11.9	0.110	3.8 (in $\text{CaCl}_2$ )	Available nutrients ( $\text{mg kg}^{-1}$ ): $N = 33.8$ , $P = 2.10$ ; electrical conductivity ( $\text{dS m}^{-1}$ ) $^d = 157$	$K_F = 1.01$ $n_F = 1.02$ $R^2 = 0.994$	$K_F = 1.20$ $n_F = 1.02$ $R^2 = 0.927$	
Isoproturon (Phenylurea)	Field soil (Sandy loam)	89.5	6.8	3.7		1.52	7.53 (in $\text{CaCl}_2$ )	Total $N$ ( $\text{g kg}^{-1}$ ) = 0.44; $P_2O_5$ ( $\text{g kg}^{-1}$ ) = 0.02; $K_2O$ ( $\text{g kg}^{-1}$ ) = 0.043  Soil microbial bio- mass carbon ( $\text{mg C}$ $\text{kg}^{-1}$ ) = 160.2	Active ingredi- ent: $K_F = 4.00$ $n_F = 0.885$ $R^2 = 0.974$ $K_{\text{loc}} = 263.3$ Commercial formulation: $K_F = 4.99$ $n_F = 0.725$ $R^2 = 0.998$ $K_{\text{oc}} = 328.3$		[122]

Simazine (Triazine)	Grassland soil (Sandy loam)	89.5	6.8	3.7	1.52	7.53 (in water)	5.94 ± 0.15	Water holding capacity (%) = 74.97 Electrical conductivity ( $\mu\text{S m}^{-1}$ ) = 87.73 Total carbon (%) = 3.10; Total nitrogen (%) = 0.34; DOC ( $\text{g kg}^{-1}$ ) = 15.25	Batch equilibrium/L and Freundlich	$K_L = 0.0037$ $q_m = 15.75$ $R^2 = 0.192$ $K_F = 0.005$ ; $n_F = 0.940$ ; $R^2 = 0.988$	[233]
Tebuconazole (Triazole)	Field soil (Sandy loam)	89.5	6.8	3.7	1.52	7.53 (in water)	5.94 ± 0.15	Total $N$ ( $\text{g kg}^{-1}$ ) = 0.44; $P_2O_5$ ( $\text{g kg}^{-1}$ ) = 0.02; $K_2O$ in ( $\text{g kg}^{-1}$ ) = 0.043 Soil microbial biomass carbon ( $\text{mg C kg}^{-1}$ ) = 160.2	Batch equilibrium/L and Freundlich	Active ingredient: $K_F = 21.9$ $n_F = 0.923$ $R^2 = 0.960$ $K_{oc} = 1,439.9$ Commercial formulation: $K_F = 30.1$ $n_F = 0.855$ $R^2 = 0.997$ $K_{oc} = 1,980.4$	[122]
Thiacloprid (neonicotinoid)	Black soil (loam)	52	42	6	61.3	7.2 (in $\text{CaCl}_2$ )	3.08	Available nutrients ( $\text{mg kg}^{-1}$ ): $N = 279$ , $P = 52.2$ ; electrical conductivity ( $\text{dS m}^{-1}$ ) <sup>d</sup> = 524	Batch equilibrium/L and Freundlich	$K_F = 9.06$ $n_F = 0.806$ $R^2 = 0.998$	[135]
Thiacloprid (neonicotinoid)	Fluvo-aquic soil (loam)	49	42	9	18.3	4.9 (in $\text{CaCl}_2$ )	1.26	Available nutrients ( $\text{mg kg}^{-1}$ ): $N = 158$ , $P = 29.6$ ; electrical conductivity ( $\text{dS m}^{-1}$ ) <sup>d</sup> = 80.1	Batch equilibrium/L and Freundlich	$K_F = 3.40$ $n_F = 0.842$ $R^2 = 0.995$	
Thiacloprid (neonicotinoid)	Paddy soil (clay loam)	32	46	22	14.2	4.4 (in $\text{CaCl}_2$ )	1.43	Available nutrients ( $\text{mg kg}^{-1}$ ): $N = 115$ , $P = 22.7$ ; electrical conductivity ( $\text{dS m}^{-1}$ ) <sup>d</sup> = 34.1	Batch equilibrium/L and Freundlich	$K_F = 4.70$ $n_F = 0.719$ $R^2 = 0.994$	

(continued)

Table 3 (continued)

Pesticide name (chemical class)	Soil content and physicochemical properties							Experimental method/ Isotherm model	Estimated parameters		Reference
	Type (texture)	% Sand	% Silt	% Clay	CEC ( $\text{cmol kg}^{-1}$ )	% OC	pH		Other information available	Sorption process	
	Red soil (clay loam)	48	34	18	11.9	0.110	3.8 (in $\text{CaCl}_2$ )	Available nutrients ( $\text{mg kg}^{-1}$ ): $N = 33.8$ , $P = 2.10$ ; electrical conductivity ( $\text{dS m}^{-1}$ ) <sup>d</sup> = 157	$K_F = 1.16$ $n_F = 0.984$ $R^2 = 0.996$	$K_D = 1.55$ $n_D = 0.943$ $R^2 = 0.989$	
	Agricultural soil	31	58	11	8.1	1.2	8.1	Calcic fluvisol devoted to different irrigated crops such as corn, tobacco, and fruit trees. $\text{CaCO}_3(\%) = 26$ Electrical conductiv- ity ( $\text{dS m}^{-1}$ ) <sup>d</sup> = 1.2	$K_F = 5.3$ ; $1/n_F = 0.60$ $R^2 = 0.989$ $K_d = 4.0$ $R^2 = 0.882$ $K_{oc} = 331$		[239]
Thiamethoxam (neonicotinoid)	Vegetable garden soil (silt loam) Depth frac- tions: • 0– 130 mm • 130– 250 mm • 250– 400 mm	19.3 23.3 18.3		10.9 (0– 130 mm)	0.31 0.14 0.08	6.85 (0– 130 mm)		Batch equi- librium/ Henry's linear	(0–130 mm): $K_d = 1.45$ ; $R^2 = 0.99$ ; $K_{oc} = 468$ (130–250 mm): $K_d = 1.19$ $R^2 = 0.99$ ; $K_{oc} = 850$ (250–400 mm): $K_d = 0.59$ $R^2 = 0.99$ ; $K_{oc} = 738$	(0–130 mm): $K_d = 0.62$ ; $R^2 = 0.93$ (130– 250 mm): $K_d = 0.34$ ; $R^2 = 0.99$ (250– 400 mm): $K_d = 0.14$ $R^2 = 0.98$	[133]
	Farm soil (fine sandy loam) Depth frac- tions:	17.0 31.3 30.3		18.9 (0– 130 mm)	0.30 0.24 0.21	6.08 (0– 130 mm)		Batch equi- librium/ Henry's linear	(0–130 mm): $K_d = 1.48$ ; $R^2 = 0.99$ ; $K_{oc} = 493$ (130–250 mm): $K_d = 0.65$ ; $R^2 = 0.98$	(0–130 mm): $K_d = 0.65$ ; $R^2 = 0.98$ (130– 250 mm): $K_d = 0.98$	



					250 mm) 6.38 (250– 400 mm)					$K_d = 1.20$ $R^2 = 0.99$ ; $K_{oc} = 500$ (250–400 mm); $K_d = 1.12$ $R^2 = 0.99$ ; $K_{oc} = 533$	$K_d = 0.49$ $R^2 = 0.93$ (250– 400 mm); $K_d = 0.60$ $R^2 = 0.96$	
					7.72 (0– 130 mm) 8.06 (130– 250 mm) 7.92 (250– 400 mm)	0.64 0.40 0.37	20.3 (0– 130 mm) 22.9 (130– 250 mm) 19.6 (250– 400 mm)	14.5 34.3 38.3	Farm soil (fine sandy loam) Depth frac- tions: • 0– 130 mm • 130– 250 mm • 250– 400 mm	(0–130 mm); $K_d = 2.03$ $R^2 = 0.99$ ; $K_{oc} = 317$ (130–250 mm); $K_d = 1.69$ $R^2 = 0.99$ ; $K_{oc} = 422$ (250–400 mm); $K_d = 1.51$ $R^2 = 0.99$ ; $K_{oc} = 408$	(0–130 mm); $K_d = 0.33$ ; $R^2 = 0.86$ (130– 250 mm); $K_d = 0.48$ $R^2 = 0.83$ (250– 400 mm); $K_d = 0.47$ $R^2 = 0.98$	

*CEC* cation exchange capacity, *OC* organic carbon, *DOC* dissolved organic carbon

<sup>a</sup>Pyz: Pyrophosphate-extractable

<sup>b</sup>Ox: Oxalate-extractable

<sup>c</sup>DCB: dithionite-extractable counterparts

<sup>d</sup>Measured in deionized water (w:v = 1:5)

decreased hysteresis coefficient of the atrazine desorption with increasing its concentration in the case of low value of initial atrazine concentration was reported by Huang et al. [57], while in the case that the initial atrazine concentration was high acted reversely, indicating that the mechanism for delaying desorption in the sorbents varied with the initial atrazine concentration.

## **3.2 *Effects of Selected Factors on Pesticide Sorption and Leaching in Soils***

### **3.2.1 *Impact of Soil Organic Matter***

Several published studies have shown that soil OM (SOM) content is regarded as one of the most crucial and predominant soil characteristics that control the extent to which sorption of organic hydrophobic molecules in natural soils happens [10, 118, 249].

As it has been well established in the relevant bibliography the chemical composition, physicochemical properties or characteristics, and nature of OM differ between soils originating from variable regions. Among the several different key factors on which the nature of SOM is dependent, the origin and age of the soil matrix, the occurring environmental conditions, and the practicable agricultural methods are included [118, 183]. For instance, according to the results a survey conducted by Xu et al. [250] regarding the carbon stabilization in aggregate fractions responding to straw input levels under different soil fertility levels it was found that varied rates of organic C occurred based on the soil fertility and plant input levels.

SOM in general consists of vegetal and animal detritus at different levels of decomposition and mineralization. SOM is correlated with the fertility of the soil as it is considered to play the primary role of the soil carbon sink, whereas its concentration varies between 1 and 6% overall. A wide range of saturated and unsaturated complex organic molecules with aromatic, aliphatic, hydrophilic, and hydrophobic substances are included in the diverse composition of SOM. Among other organic compounds carbohydrates, fats, lignins, proteins, and humic substances (fulvic acid (FA), humic acid (HA), and humin) are included. The allocation of contained functional groups (oxygenated: -OH, -COOH, -C=O, -C-O-C-, -C-O-O-C, etc.; nitrogen containing amine and amide: -NH<sub>2</sub>, -NH, aromatic ring, etc.) which act as sites of adsorption determine and regulate the degree of pesticides' sorption on the soil surface and therefore the leaching behavior of pesticides into aquifers.

The recent findings of the study conducted by Wang et al. [62] regarding the FT-IR spectra characterization of soil-derived dissolved organic matter (DOM) for the investigation of atrazine binding during the sorption process onto black soil indicated that main compositions of soil DOM among others mainly contained proteins, polysaccharides, and humic substances that significantly enhanced the adsorption efficiency of atrazine by soil.

Numerous studies have shown that a positive correlation between SOM and adsorption coefficient values, for instance for alachlor ( $R^2 = 0.80$ ) [42] ( $R^2 = 0.87$ ) [43], carbendazim ( $R^2 = 0.77$ ) [94], chlorpyrifos ( $R^2 = 0.82$ ,  $p < 0.001$ ) [119], endosulfan ( $R^2 = 0.96$ ) [168], flucetosulfuron ( $r = 0.910$ ) [174], iodosulfuron ( $R^2 = 0.87$ ) [197], and triasulfuron ( $r = 0.987$ ) [246].

In order to estimate the influence of SOM quality in the abamectin and atrazine  $K_{OC}$  values the quality of contained HAs was analyzed by Novotny et al. [35] through the means of  $^{13}\text{C}$  solid state Nuclear Magnetic Resonance ( $^{13}\text{C}$  NMR) and Principal Component (PC) Regression. Negative loadings for aliphatic compounds and positive loadings for aryl C, typical of partially oxidized pyrogenic C were reported. Because no correlation between  $K_F$  values and SOM was observed, the normalized by OC values ( $K_{OC}$ ) were obtained that varied within the range of 1,100–11,400  $\text{mL g}^{-1}$  for abamectin and 30–150  $\text{mL g}^{-1}$  for atrazine. The SOM content was not enough to explain the wide  $K_{OC}$  variation, whereas on the contrary the chemical structure of SOM could. Acquired results showed strong correlation of HAs with the abamectin  $K_{OC}$  values ( $R^2 = 0.91$ ,  $p < 5 \cdot 10^{-8}$ ) and weaker with atrazine  $K_{OC}$  ( $R^2 = 0.63$ ,  $p < 0.0001$ ), in addition to a smaller standardized slope for abamectin than for atrazine (1.01 and 0.76 respectively), which were explained by the higher hydrophobicity of abamectin, being thus more prone to interact with the polycondensed aryl groups from the pyrogenic C.

According to Parolo et al. [118], who investigated the sorption behavior of the nonionic pesticide chlorpyrifos on 12 representative natural soils of the North Patagonian Argentinian region the process of sorption was mainly affected by soil aliphatic components that were measured by FT-IR analysis on the whole soil samples. The values of normalized by the organic carbon (OC) content sorption coefficients varied between 9,000 and 20,000  $\text{L kg}^{-1}$  (for %OC content 1.25–6.82), while a significant relationship between chlorpyrifos sorption ( $K_{OC}$ ) and the variables pH and A/B height band ratio (band A: aliphatic components, 2,947–2,858  $\text{cm}^{-1}$  and band B: hydrophilic components, 1,647–1,633  $\text{cm}^{-1}$ ) was found and reported ( $R^2 = 0.66$ ). Based on the derived model,  $K_{OC} = 22,757 + 4,364 \text{ A/B} - 1,564 \text{ pH}$ , it was observed that the ratio of the peaks' height A/B seemed to influence favoring sorption whereas on the contrary soil pH seemed to have a significant opposite effect on sorption.

Recently, a positive correlation was reported by Mendes et al. [183] among SOM, clay content, and sorption  $K$  values of tebuthiuron and hexazinone in soil samples taken from an agricultural area of São Paulo, Brazil. The values of sorption coefficients  $K$  for the two tested pesticides after using the batch equilibrium method ranged from 1.2 to 2.9  $\text{mL g}^{-1}$  for tebuthiuron and from 0.4–0.6  $\text{mL g}^{-1}$  for hexazinone, respectively.

Humic substances and their relation to the sorption of eight selected agricultural pesticides (atrazine, carbaryl, flumioxazin, hexazinone, imidacloprid, MCPA, metsulfuron-methyl, and terbuthylazine) in eight volcanic soils that differed in the fulvic and humic constituents of their OM were evaluated by Alister et al. [50] and published results of their study indicated that HA content regulated the sorption between pesticide and soil, especially through the carboxylic groups.

The study of Gaonkar et al. [115] focusing on the evaluation of soil organic amendments and their impacts on the sorption of organophosphate pesticides on an alluvial soil highlighted that the net effect of the application of organic amendments was an increase in the sorption of two selected organophosphates, dichlorvos, and chlorpyrifos that depended on both the nature of DOM and pesticide properties, whereas according to the spectroscopic characterization large amounts of highly humified and aromatic material were mainly contained in used organic amendments.

The significance that SOM has in the environmental fate of acetamiprid, as well as the investigation of the interactions between acetamiprid and three fractions of humic substances was surveyed by Murano et al. [38] by performing batch equilibrium experiments by using various combinations of a field soil sample and three different fractions prepared (HAs, FAs, and humin isolated from the same soil). Based on the reported Freundlich isotherm constant values for the tested fractions ( $K_F$ : 6.100 for humin, 4.179 for HAs and 4.756 for FAs) interactions of hydrophobic nature between humin and HAs or FAs were revealed, in which their dissociated carboxyl and phenolic groups became oriented to face the soil solution.

The influence of soil organic components determined by  $^{13}\text{C}$  CP/MAS NMR spectroscopy on the sorption of chlorpyrifos was assessed by Savini et al. [119] who reported that whereas aryl C relative proportion was positively correlated with  $K_{OC}$  values, on the contrary, the correlation between alkyl C and O-aryl C proportions with  $K_{OC}$  data is negative ( $R^2 = 0.82$ ,  $p < 0.001$ ).

According to the research of Ćwieląg-Piasecka et al. [90] who compared the effect of two types of organic sorbents, HAs, and biochar, on the sorption-desorption processes of different polar pesticides (carbamates, phenoxyacetic acids, and aniline derivatives), the investigated HA exhibited high affinity to polar, ionic pesticides of high water solubility, which were adsorbed via specific interactions with HA functional groups. Specifically, HAs exhibited strong affinity for the ionic substances (percentage uptakes: 74.6 and 67.9% initial dose of 2,4-D and MCPA, respectively) and much weaker retention of nonionic carbamates (35.4% of carbofuran and 10.2% of carbaryl sorbed).

The published work of Chitolina et al. [184] investigating the Influence of soil depth on sorption and desorption processes of hexazinone revealed that the small differences that were observed in OC content between soil depths (of 0–10, 10–20, and 20–30 cm) affected hexazinone retention and the corresponding decreasing order of determined Freundlich coefficients ( $K_F$ ) values were 0.18, 0.11, and  $0.08 \text{ g}^{(1-1/n)} \text{ L}^{1/n} \text{ kg}^{-1}$ .

Furthermore, the impact of exogenous OM (composted sheep manure) on the sorption and leaching of boscalid, flonicamide, myclobutanil, and penconazole pesticides was assessed by Pérez-Lucas et al. [82] and the obtained results of the conducted equilibrium experiments on an agricultural soil (SE Spain) showed that the sorption capacity of amended soil was significantly increased in all cases minimizing their potential for groundwater pollution. In addition, leaching experiments indicated with amended soil columns significantly limited the vertical movement of the pesticides in leachates especially for the cases of boscalid and penconazole.

### 3.2.2 Impact of Soil Inorganic Components

Minerals and rocks are the predominant inorganic soil components that are formed through lithogenesis and subjected to further diverse changes that are dependent on several factors and processes such as diagenesis, metamorphism, erosion, deposition, weathering, and transport [251]. The average chemical constituents of minerals (as natural inorganic compounds of Earth's crust) are oxygen (50% w/w), Si (25% w/w) and mainly  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ , and  $\text{K}^+$  cations (the rest 25% w/w) [251].

According to the overviewed data of the present study the clay minerals group (kaolinites, smectites, vermiculites, illites, and chlorites) has been demonstrated as the most important inorganic fraction for the sorption of synthetic pesticides. Inorganic portion of soil that is mainly the clay fraction contained in cases of soil matrices which are characterized with low OM contents is very important for the adsorption process of organic pesticides [110]. Therefore, apart from the SOM that has by definition high compatibility and strong association affinity for many non-polar pesticides (thus offers adsorption sites for such molecules especially into soils with >3% OM) clay minerals also play an important role and have a substantial contribution to the process of sorption, specifically in the case of polar pesticides and soils and sediments with low OM content [252].

A wide diversity of mechanisms through which pesticides can be (ad)sorbed from soil/water systems on soil clay mineral has been reported in the relative bibliography, including H bonding, hydrophobic bonding, van der Waals interactions, anion exchange, cation exchange, and ligand exchange pathways [244].

The effects of clay content in soil on the sorption process of two organophosphorus pesticides diazinon and chlorpyrifos were examined by Copaja et al. [110] in a natural soil sample (Chile) and in a soil modified with clay addition (1% of kaolinite or/and montmorillonite). Acquired results showed that the addition of both clays into the soil resulted in increased amounts of both pesticides retained in the soil and hence lowered the possible contamination of the groundwater.

These results are in accordance with the positive correlation that was found and reported by Mendes et al. [183] among clay content, SOM, and tebuthiuron and hexazinone sorption  $K_d$  values (in the range of 1.2–2.9 mL g<sup>-1</sup> and 0.4–0.6 mL g<sup>-1</sup>, for tebuthiuron and hexazinone, respectively).

The results of Bošković et al. [169] who conducted a study concerning the adsorption of the two conazole fungicides (epoxiconazole and tebuconazole) in 20 soils from the Czech Republic in relation to soil properties were very interesting. More specifically, among the “basic” (TOC, pH, clay), “advanced” (surface area, minerals) soil properties, and  $K_d$  coefficients that were evaluated in the multivariate analysis revealed for both fungicides a strong negative correlation with soil pH, and a lower positive correlation with soil organo-mineral complex (by means of TOC, clay, and surface area) and C and N in SOM. No correlation of adsorption parameters with particle sizes or CEC was observed.

According to the published data of Kumari et al. [174], regarding the investigation of the adsorption-desorption and leaching of the sulfonylurea herbicide flucetosulfuron in three Indian soils the acquired  $K_F$  exhibited positive correlation with OC content ( $r = 0.910$ ) and clay content ( $r = 0.746$ ). On the contrary a negative correlation with soil pH ( $r = -0.635$ ) was revealed.

The statistical multivariate tests conducted in the survey of Sidoli et al. [211] regarding the adsorption data of the herbicide S-metolachlor and two of its metabolites (metolachlor ethane sulfonic acid and metolachlor oxanilic acid) on 17 surface soils and three geological solids related the highest  $K_d$  values for the herbicide S-metolachlor with the soils and geological solids with the highest OC and clay-fraction contents. Similarly, the sorption values of the new insecticide cyantraniliprole in different types of soils (Russia) were studied by Kolupaeva et al. [137] via the batch equilibrium method and obtained  $K_{OC}$  closely correlated with the OC and clay contents.

In a recent survey of Agbaogun et al. [103] on the adsorption behavior of five phenylurea herbicides by tropical soils (18 differently composed soils originating from southwestern Nigeria) statistically significant correlations (Pearson) were delivered between sorption parameters ( $K_d$ ,  $K_f$ , and  $n$ ) and specific soil and herbicide properties, among which pH, CEC, OC content, content of amorphous Fe and Mn oxides, clay/silt mass proportions, as well as molecular descriptors of octanol-water partition coefficient ( $\log K_{ow}$ ) and molecular mass (MW) of the moderately hydrophobic herbicides, were included. Furthermore, the estimated  $K_{d, \text{mineral}}$  values of diuron (2.71), linuron (1.98), monuron (0.85), chlorotoluron (0.59), and isoproturon (0.56) reported in the same survey indicated that  $K_{d, \text{mineral}}$  contributed between 15 and 40% to the  $K_d$  average reported for these compounds, a fact that is implying that soil mineral fractions, vis-à-vis clay minerals, and the amorphous metal oxides, also contributed fairly significantly (about 15–40%) to the sorption of the five test compounds in the soils. Moreover, the intercorrelations between the basic properties of the soils used in this study revealed that extractable Fe and Mn oxides are significantly high and positive correlated with clay and silt contents and negative correlations with sand content [103].

Hiller et al. [201] tested the adsorption of Na-K-DMA MCPA salt (dimethyl ammonium-potassium-sodium salt of (4-chloro-2-methylphenoxy)acetic acid) on three agricultural soils by using column experiments and demonstrated the effect of clay and OC content on Na-K-DMA MCPA salt sorption despite the fact that small number of soil samples were tested. In a previously published survey of Peng et al. [247] both clay content and OM of soils were found to be important factors affecting the adsorption of triflumezopyrim in water-soil environment system. In the study of Rodríguez-Liévana and Peña [146] examining the adsorption-desorption capacity of dimethenamid and fenarimol onto three agricultural soils and how these processes are affected by treated wastewater and fresh sewage sludge-derived dissolved OC reported that in the case of fenarimol's adsorption by the soil OC content seemed to be the major factor controlling the process, whereas in the case of the adsorption of dimethenamid the mineral fraction played the key role, especially in the matrix where clay:organic content ratio was high.

In a work of Marín-Benito et al. [26] studying and comparing the effect on the mobility of ethofumesate and terbutryn in soils and two organoclays (swelling and non-swelling clays modified with octadecyltrimethylammonium) was observed that the effect of the organoclay barriers was more significant for ethofumesate, whereas for terbutryn the effect of organoclays was close to that of certain organic residues. The effect of soil organo-inorganic compounds different in particle size on butachlor sorption was surveyed by Huang et al. [87] and results showed that the clay fraction was the highest in butachlor adsorption capacity but the lowest in desorption rate, while the sand fraction was the lowest in adsorption capacity but the highest in desorption rate. The published results of Ahmad [238, 246] regarding a pedospheric sorption investigation of the sulfonyl urea herbicide triasulfuron via regression correlation and regression analysis in selected soils gave a positive correlation between  $K_d$  and clay content ( $r = 0.980$ ).

In the study of Prado et al. [166] regarding the mobility of the pesticide 2,4-D in clay soils it was concluded that the preferential flow caused by both high clay content and the presence of macrofauna pores significantly reduced the buffering capacity of the soil, increasing the risk of contamination by herbicides of the underlying aquifer. The addition of synthetic clay (oleate-modified hydrotalcite) by Gámiz et al. [207] to an agricultural soil affected the sorption, leaching, persistence, and enantiomeric composition of soil residues of two chiral fungicides, tebuconazole and metalaxyl. Specifically, the addition of clay at a rate of 1% increased metalaxyl soil sorption coefficient ( $K_d$ ) from 0.34 to 3.14 L kg<sup>-1</sup> and that of tebuconazole from 2.4 to 47.4 L kg<sup>-1</sup>.

Based on the regression equation that was proposed Gao et al. [231] for the sorption prediction of pymetrozine on six different soil samples:  $\log K_F = 4.3708 - 4.5709 \times \log(\text{pH in } 0.01 \text{ mol}\cdot\text{L}^{-1} \text{ CaCl}_2) + 0.4700 \times \log \text{OC } \% + 0.0057 \times \text{sand } (\%) + 0.0022 \times \text{CEC (clay)}$ , with  $R^2 = 0.9982$ , the clay content of soil positively affected the sorption of pymetrozine.

According to the findings of current review it is observed most of the found and overviewed articles investigating how soil inorganic minerals can affect the adsorption-desorption behavior of pesticides in the soil is focused mainly on crystal silicate clay mineral (for example, montmorillonite and kaolinite), while on the opposite the scientists focusing on soil metal oxides, such as iron oxides, aluminum oxide, are much less in number. In this direction of research was the study of Huang et al. [57] on the effects of amorphous Fe oxides on adsorption-desorption of atrazine in soil. Based on the conclusions of the study amorphous Fe oxides with relatively high specific surface area and relatively big number of protons donating functional groups demonstrated a relatively high sorption capacity and affinity for atrazine even though their complexation with SOM contained in natural soil inhibits their direct adsorption capacity.

The role of soil iron oxides (IOs) in the distribution and interactions of pentachlorophenol in soils was investigated by Diagboya et al. [225] and batch sorption studies were conducted on whole soils and soils selectively treated to remove IOs (IOR) and OM (OMR). As revealed by the kinetic models, sorption equilibrium occurred faster in the IOR soils than the untreated and OMR soils and therefore iron

oxides played greater roles in the sorption of pentachlorophenol than the OM content.

The influence of Al-oxide on pesticide sorption to woody biochars with different surface areas (SA) was investigated by Shou et al. [199]. The published results of this survey revealed the enhanced sorption of the pesticide isoproturon to the Al-oxide-treated low-SA biochar that was positively related to the increased mesopore area.

### 3.2.3 Impact of Pesticides' Physicochemical Properties

The chemical structure of a pesticide and some specific characteristics of its molecules determine its sorption behavior and its affinity to be sorbed on soil colloids. The nature of functional groups contained in the compound is a crucial factor. Several functional groups such as carboxyl, carbonyl, alcoholic and amino moieties are very important as they govern the process of binding. Enhanced adsorption capacity has been observed with the presence of the below functional groups in pesticides molecules in the increasing order:  $R_3N^+$ ,  $-\text{CONH}_2$ ,  $-\text{OH}$ ,  $-\text{NHCOR}$ ,  $-\text{NH}_2$ ,  $-\text{OCOR}$ , and  $-\text{NHR}$  [18]. Especially the ability of amino group to be protonated (which is a property dependent on pK value of the molecule) leads to the sorption as cations, and thus is very important. Moreover, the participation of amino and carbonyl moieties into hydrogen bonding has also been revealed [18].

A study on the soil sorption of six basic (pirimicarb, pirimiphos ethyl, prochloraz, prometryn, quinoxifen, and triadimefon), and six neutral ( $\alpha$ -endosulfan, chlorpyrifos, fenthion, parathion, parathion methyl, and cis permethrin) pesticides was conducted by Vitoratos et al. [123] and based on the experimental data that were acquired hydrophobic, electrostatic, and polar interactions were implied.

The charge characteristic of pesticides, the equal or unequal distribution of electrons in its molecule producing temporary or permanent polarity, correspondingly, its weak or strong tendency to donate or adopt protons are only some of the pesticide properties that determine the mobility of pesticides into the soil-water bulk systems.

The sorption behavior of both ionizable and nonionizable pesticides in the presence of HA in soils was investigated by Ćwieląg-Piasecka et al. [90] and high affinity of investigated HA to polar, ionic pesticides of high water solubility, which are sorbed via specific interactions with HA functional groups.

Moreover, water solubility and hydrophobicity or lipophilicity, expressed with means of octanol/water partition coefficient ( $K_{ow}$  or  $\log K_{ow}$ ), are two of the most important physicochemical properties whose impacts on the sorption have been evaluated in several scientific surveys [20, 28, 122, 134]. Rodríguez-Liébaña et al. [138] evaluated the adsorption behavior of six different pesticides ( $\alpha$ -cypermethrin, deltamethrin, pendimethalin, thiacloprid, dimethenamid, and fenarimol) that differed in hydrophobicity (range of  $\log K_{ow}$  values: 1.26–5.8) in three organic poor soils (% OC content  $\leq 1.2\%$ ). Obtained results indicated lower kinetic rates for the more hydrophobic pesticides ( $\log K_{ow} \geq 4.6$ ) compared with the other compounds under



study. According to the intraparticle diffusion model that was used, a strong contribution of a rapid initial adsorption on soil surface for thiacloprid, dimethenamid, and fenarimol was observed, while moderate contribution for the hydrophobic pesticides was achieved.

### 3.2.4 Impact of Carbon-Rich Organic Amendments Applied to Soils

Numerous recent studies have confirmed the advantages and benefits that are gained in the improvement of soil characteristics (including fertility, adsorption capacity, leaching and remediation by the reduction of the contamination of the neighboring terrestrial and aquatic areas) after the application of a wide variety of carbon-rich by-products (which are known with the term biochar) that are prepared by the application of the pyrolysis technique on low cost by-products, agrowastes, and organic materials under high temperatures in the absence of oxygen [14, 16, 84]. Several different functional groups present in the structure of these biochars play an important role and lead to a stronger adsorption of the organic pesticides' molecules. In general, it is well known that under higher temperature of pyrolysis the produced biochars have more aromatic units and pores for capturing more sorbates.

According to the results of Chin-Pampillo et al. [84], the addition of three different pyrolyzed agrowastes of pineapple stubble, palm oil fiber and coffee hull, as amendments in a tropical soil it was observed that the sorption behavior and persistence of bromacil and diuron was affected. More specific, the two first amendments resulted in an increase of bromacil's sorption of three to four-fold and a three to six-fold change in diuron's sorption, while the addition of the third biochar had little effect. Similarly, the published results of a survey conducted by Aldana et al. [67] on the effects of biochar addition on the leaching and sorption of the agrochemicals atrazine, diuron, enrofloxacin, oxytetracycline, and tetracycline in tropical soils showed that sorption was higher in biochar-amended soils than soils without biochar amendment and the used biochars were produced from mixed softwood, rice husk, and miscanthus straw, after pyrolyzed at 700°C.

In a recently published study of Cheng et al. [233] it is reported that overall the application of biochar in agricultural soils combined with arbuscular mycorrhizal fungi inoculation can influence the decomposition and leaching of simazine, mitigate its accumulation in the topsoil, and consequently reduce the availability of the studied pesticide. Based on the findings of a review conducted by Siedt et al. [249] regarding the comparison of straw, compost, and biochar on the fate of pesticides in agriculture soils it is concluded that although biochar has the higher effectiveness of all in increasing the sorption capacity of soils however it cannot surpass straw and compost regarding the other aspects investigated (such as transformation and retention of nutrients, soil microbial communities, etc.). The impact of biochar addition to soils and sediments samples from four sites along Litani river basin on the adsorption behavior of three commonly used herbicides fluazifop, terbuthylazine, and triclopyr was assessed by Kchour et al. [173] and based on the derived results of the survey  $K_{ads}$  values in biochar treated matrices increased

considerably in comparison with the non-treated ones. Furthermore, according to the same study in the presence of biochar the phenomenon of sorption was not reversible, and hysteresis occurred.

Bentazone sorption and desorption studies executed by Ponnam et al. [74] revealed that the introduction of biochar not only improved several characteristics of the soil among which pesticide adsorption efficiency is included (pH, CEC, electrical conductivity), but also that lowered the desorption levels and thus enhanced soil quality. In a separate survey, Ponnam et al. [95] reported the same pattern of attitude for the case of carbofuran that was irreversibly sorbed by moderately acidic soil amended with biochar. The effects of raw feedstock and biochar (produced from soybean residues, sugarcane bagasse, and wood chips (grape)) amendments on sorption-desorption and leaching potential of the pesticides aminocyclopyrachlor, metolachlor, and imidacloprid were studied by Mendes et al. [47], and decreased availability of metolachlor and imidacloprid in soil was observed via increased sorption process. For the case of aminocyclopyrachlor the availability differed between the use of raw feedstock and biochar, while the most important impact on pesticide behavior was derived from biochar produced from wood chips pyrolysis. Reduced dissipation of thiamethoxam in a biochar-amended agricultural soil was reported by You et al. [242].

Numerous published data during the period 2016–2021 have demonstrated the increased adsorption efficiencies that were achieved (and possible lower pesticide leaching mitigation) after biochar amendments applied on different soils and for several pesticides, such as for acetamiprid [39], acetochlor [40], atrazine in the presence of Cd(II) [52] or not [60, 63, 64], bentazone [75, 77], boscalid [75, 77], cadusafos [88], carbaryl [90], carbofuran [90], chlorothalonil [109], chlorpyrifos [116, 117], clomazone [80], clothianidin [136], difenoconazole [143], 2,4-dichlorophenoxyacetic acid (2,4-D) [90], diuron [117, 148], fenamiphos [88], glyphosate [117, 180, 182], imazapic [190], imazapyr [190], imazamox [189], imidacloprid [63, 136], isoproturon [63], 4-chloro-2-methylphenoxyacetic acid (MCPA) [90, 120], metalaxyl [206, 207], metolachlor [90, 214], picloram [189], pyrimethanil [75, 77], simazine [235, 253], tebuconazole [207], terbuthylazine [189], and thiacloprid [136, 240, 241].

The published results of Ćwieląg-Piasecka et al. [90] who examined the biochar as specific sorbents of several carbamate, phenoxyacetic acids, and aniline derivatives pesticides indicated that the biochar that was produced from wheat straw and used in the study preferentially attracted nonionic pesticides with relatively high log  $K_{ow}$  values and low water solubility probably because of its moderately hydrophobic character. Therefore, the principal mechanism of pesticides' attraction to biochar that was proposed was the hydrophobic bonding.

According to the findings of García-Jaramillo et al. [69], the role of biochar and biochar water-extractable substances on the sorption of pesticides onto soils is depended on soil and biochar properties and time of application, and these parameters need proper consideration before the application because reduction or increase in the mobility of ionizable organic compounds may occur. That was based on their observation that, in spite the enhanced soil sorption capacity of the herbicides

azimsulfuron and penoxsulam that was observed after the application of raw biochar as soil amendment in two rice paddy soils, on the contrary, lessened azimsulfuron adsorption was reported in the washed biochar soil samples than in the washed biochar. This was attributed possibly due to the reduction of polar groups of biochar through washing step, which had no effect on penoxsulam adsorption.

### 3.2.5 Impact of Pesticide Mixture Interactions

It has been well documented that the co-presence of pesticides in chemical mixtures promotes changes in its behavior into soil due to synergistic or antagonistic phenomena that may occur [147, 153, 160].

The leaching of three selected pesticides, diuron, hexazinone, and sulfometuron-methyl, applied in soils with contrasting textures (sandy or clayey) and by two different modes, alone and in mixture was investigated by Dos Reis et al. [160]. The results of soil column experiments showed that when herbicides were applied in mixture of the commercial mixture diuron + hexazinone + sulfometuron-methyl, interactions among them could potentially promote changes in herbicide behavior in the soil. Hexazinone was reported to have the greater leaching potential and mobility along the soil profile compared to the other two studied molecules, whereas diuron remained at the top layer of the soil, and hence indicated that this herbicide has low soil mobility.

In a similar study conducted by Sousa et al. [153] regarding the sorption and desorption of diuron, hexazinone and their mixture in soils with different attributes it was revealed that in all tested soils, diuron and hexazinone showed higher sorption coefficients  $K_F$  values when mixed. Carneiro et al. [147] surveyed the way that herbicide mixtures can affect the adsorption processes in soils under sugarcane cultivation. For that purpose, the sorption process of diuron, hexazinone, and sulfometuron-methyl in isolated and mixed conditions was examined. Results of the study refer that herbicide mixtures reduced the maximum adsorption ( $q_e$ ) in  $\approx 50$  (diuron), 56 (hexazinone), and 55% (sulfometuron-methyl) compared to isolated tests. Also, herbicide mixtures reduced the sorption rate ( $K_F$ ) 24 (diuron), 89 (hexazinone), and 66% (sulfometuron-methyl) compared to conditions isolated tests.

## 4 Conclusions and Future Perspectives

Regardless of their mode of application several different pesticide compounds that are unavoidably used in the terrestrial environment mainly for agricultural purposes (protection of crop quality and quantity) reach the soil and are subjected to biotic and abiotic processes which affect their distribution and transportation into the soil-water-biota systems. Binding to soil particles, known as sorption, desorption into the soil bulk, and vertical removal from topsoil into lower subsoil depths by leaching

are unquestionably the predominant abiotic phenomena that influence their behavior and bioavailability into these ecosystems.

According to the findings of the current overview a great number of publications, overall 228 reports, have been found for the period 2016–2021 (from 01/01/2016 to 30/06/2021) regarding the sorption, desorption, and leaching of several different pesticides which belong to a wide variety of chemical groups. Obtained data revealed that the evaluation of adsorption/desorption capacity on soil, leaching, and transportation process for 186 individual pesticides, in total, have been investigated and reported in the scientific literature published in the last 5.5 years. Moreover, atrazine (triazine herbicide) is the pesticide on which scientific interest has been focused, followed by chlorpyrifos (organophosphorus insecticide), imidacloprid (nicotinoid insecticide), glyphosate (organophosphorus insecticide), and metolachlor (systemic fungicide). Results showed that the scientific interest has been focused either on the most used and thus frequently detected pesticides or/and on the pesticides that exhibit the longer half-lives and can remain in the water and soil at high levels (above several hundreds of  $\mu\text{g L}^{-1}$  or  $\mu\text{g kg}^{-1}$ ) and therefore pose a higher ability to threaten exposed ecosystems and humans through the food chain.

Different sorption, desorption, and leaching attributes, behaviors, affinities, and characteristics were observed within the overviewed data indicating that the transportation and distribution fate of applied pesticides is dependent upon the combination of the studied soil/pesticide system. In general, among the most important soil factors that can affect the studied processes both OM and clay contents were included, whereas soil pH and CEC played a secondary role. Extended research concerning the enhancement of pesticide sorption and reduction of leaching into aquifers by a variety of different biochar amendments has been conducted.

A knowledge gap concerning the impact of pesticide mixture interactions on the adsorption on soils' colloids, leaching potential, and mobility of pesticides along the soil profile is observed, as the overviewed surveys examining this topic are very scarce. Therefore, more surveys in this direction must be conducted in future research, since it is indisputable fact that chemical cocktails can promote variations in the behavior of individual pesticide compounds into the soil via possible and simultaneous synergistic or antagonistic phenomena.

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