The Handbook of Environmental Chemistry 113

Series Editors: Damià Barceló · Andrey G. Kostianoy

M. Sonia Rodríguez-Cruz
M. Jesús Sánchez-Martín *Editors*

Pesticides in Soils

Occurrence, Fate, Control and Remediation

Springer

The Handbook of Environmental Chemistry

Volume 113

Founding Editor: Otto Hutzinger

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Pesticides in Soils

Occurrence, Fate, Control and Remediation

Volume Editors: M. Sonia Rodríguez-Cruz ·
M. Jesús Sánchez-Martín

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Series Preface

With remarkable vision, Prof. Otto Hutzinger initiated *The Handbook of Environmental Chemistry* in 1980 and became the founding Editor-in-Chief. At that time, environmental chemistry was an emerging field, aiming at a complete description of the Earth's environment, encompassing the physical, chemical, biological, and geological transformations of chemical substances occurring on a local as well as a global scale. Environmental chemistry was intended to provide an account of the impact of man's activities on the natural environment by describing observed changes.

While a considerable amount of knowledge has been accumulated over the last four decades, as reflected in the more than 150 volumes of *The Handbook of Environmental Chemistry*, there are still many scientific and policy challenges ahead due to the complexity and interdisciplinary nature of the field. The series will therefore continue to provide compilations of current knowledge. Contributions are written by leading experts with practical experience in their fields. *The Handbook of Environmental Chemistry* grows with the increases in our scientific understanding, and provides a valuable source not only for scientists but also for environmental managers and decision-makers. Today, the series covers a broad range of environmental topics from a chemical perspective, including methodological advances in environmental analytical chemistry.

In recent years, there has been a growing tendency to include subject matter of societal relevance in the broad view of environmental chemistry. Topics include life cycle analysis, environmental management, sustainable development, and socio-economic, legal and even political problems, among others. While these topics are of great importance for the development and acceptance of *The Handbook of Environmental Chemistry*, the publisher and Editors-in-Chief have decided to keep the handbook essentially a source of information on "hard sciences" with a particular emphasis on chemistry, but also covering biology, geology, hydrology and engineering as applied to environmental sciences.

The volumes of the series are written at an advanced level, addressing the needs of both researchers and graduate students, as well as of people outside the field of "pure" chemistry, including those in industry, business, government, research establishments, and public interest groups. It would be very satisfying to see these volumes used as a basis for graduate courses in environmental chemistry. With its high standards of scientific quality and clarity, *The Handbook of Environmental Chemistry* provides a solid basis from which scientists can share their knowledge on the different aspects of environmental problems, presenting a wide spectrum of viewpoints and approaches.

The Handbook of Environmental Chemistry is available both in print and online via https://link.springer.com/bookseries/698. Articles are published online as soon as they have been approved for publication. Authors, Volume Editors and Editors-in-Chief are rewarded by the broad acceptance of *The Handbook of Environmental Chemistry* by the scientific community, from whom suggestions for new topics to the Editors-in-Chief are always very welcome.

Damià Barceló
Andrey G. Kostianoy
Series Editors

Preface

The occurrence of pesticides in soils has raised a considerable environmental concern because the use of mobile and/or persistent compounds affects both soil and water quality. This is particularly important when considering the increased contamination of water sources by pesticides in agricultural areas around the world.

Nowadays, productive agrosystems are usually looking to obtain a high yield in the shortest possible time. This model of agriculture which is defined as intensive or conventional is based on an excessive soil tillage and irrigation that has an important environmental cost. For this reason, conservative cropping systems involving changes in the soil management and/or the agricultural practices are being implemented in the last decades with a view to solve or minimize their negative consequences, ensuring the sustainability of agrosystems and decreasing environmental pollution.

However, the use of pesticides continues to be necessary, to a greater or lesser extent, even in conservation agriculture practices, because farmers consider pesticides to be essential compounds for increasing crop yield by controlling the pests and diseases that threaten the food supply. Therefore, there is a need to combine conservation agriculture and the use of pesticides to preserve soil health and quality without giving up high crop yield. This involves understanding the fate of pesticides applied to assess and minimize their potential environmental risk to soil and water quality.

The processes that control the fate of these compounds in soils, including adsorption, leaching and degradation, have been evaluated in different studies under laboratory and field conditions although this fate is generally studied when applying conventional practices. Field experimental data on pesticide dynamics in soils under conservative agricultural practices, such as the application of organic amendments or conservation tillage systems, as well as their modelling, which are less frequent, are also evaluated in this book. Data obtained under real conditions are required to design an environmentally safe and effective application, and subsequently model pesticide behaviour in order to predict its persistence, dissipation and/or mobility under these agricultural practices. In addition, the potential toxicity of pesticides on soil microorganisms will be examined since soil microorganisms are known as the growth engines of terrestrial ecosystems by controlling key reactions in nutrient cycling related to soil fertility. There is an urgent need for revisiting the current framework regarding pesticide toxicity on soil microorganisms, especially in light of the major methodological advances that have occurred in soil microbiology in the last 15 years.

Furthermore, this book provides information on the presence of residues of compounds as currently used pesticides in agricultural soils around the world and address in depth different aspects of pesticide fate. The transport and distribution processes which take place in soil environment are examined for pesticides and for chiral compounds. The bioavailability and persistence of pesticides are evaluated in the presence of dissolved organic matter of soil when organic amendments are applied to soil or into field systems when best practices aim to mitigate their migration towards surface water. The influencing factors for the pesticide residues uptake by plants are also addressed.

Moreover, different physicochemical and biological technologies or biopurification systems as biotechnological tools developed in recent years aiming at immobilizing and degrading pesticides are included and discussed considering they may prevent soil and water pollution or to minimize the environmental exposure to pesticides.

The book is aimed at a broad audience of researchers, including environmental chemists and engineers, ecologists, together with other professionals responsible for soil management, and decision-makers. The volume contributions concerning the environmental implications of the presence of pesticides in soils to assess their impact on soil quality, the fate of these compounds at laboratory and field scale across different soil types, the evaluation of the impact of these compounds on the soil microbial communities, as well as soil contamination prevention and remediation studies make this book useful for anyone with an interest in the soil environment.

Finally, we would like to thank all the contributing authors for their efforts in preparing this comprehensive compilation of research papers. Special thanks to Dr. Damia Barceló (Series Editor), Dr. Sofia Costa (Associate Editor) and Ms. Ramya Venkitachalam (Project Coordinator for Springer Nature), who helped us during the process.

Salamanca, Spain M. Sonia Rodríguez-Cruz
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Currently Used Pesticides' Occurrence in Soils: Recent Results and Advances in Soil-Monitoring and Survey Studies

Shiva Sabzevari and Jakub Hofman

Contents

Abstract The hazardous effects of pesticides on the ecosystem are indisputable. Many studies have been devoted to the monitoring of pesticides and their occurrence in various systems and the adverse effects that they impose on different parts of the environment. However, most of the efforts have been dedicated to very persistent chlorinated compounds. Other compounds such as currently used pesticides (CUPs) have not been given appropriate attention. To clarify the situation regarding recent investigations in the field of monitoring CUPs in the soil, we performed a review of the studies which have been carried out in the last 5 years worldwide. This review makes clear an acute need for bringing the status of CUPs in the soil to greater consideration and shows the current shortcomings of actions towards monitoring CUPs in soil all around the world.

Keywords Currently used pesticides, Occurrence, Soil monitoring, Transformation products

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1 Introduction

The importance of pesticides to agricultural production is vital, because without them crop yields would be beset by great loss and would be insufficient for the world's growing population. Even with current advancements in agricultural science and technology, 10–90% of all food and fibre crops are lost due to pests, diseases, weeds, and birds [1]. During the years 2015–2018 the application of pesticides on farmlands around the world was 2.65 kg ha^{-1} on average, which showed an increase in comparison with the year 2000 when the figure was 2.07 kg ha^{-1}, and moreover it stood at 1.7 times higher than the amount applied in 1990 [2]. These statistics confirm the increasing use of pesticides over the last decades. Global annual pesticide use in agriculture has increased since the emergence of these substances, yet in the last decade it has increased with gentler slope. From 2015, less than a 0.5% increase in the pesticide use has been recorded each year, and in 2018 – with 0.7% drop comparing to the previous year – it amounted to 4.1 million tons among all the regions. Asia had the highest annual use of pesticide with an average of about 2.1 million tons during the years 2015–2018 [3].

Alongside the beneficial effects that different types of pesticides bring, these chemicals can have destructive toxic effects on non-target organisms even more than on target organisms, and thus they can impact ecosystem biodiversity [4]. Many of these organisms play crucial roles in the ecosystem, including decomposing organic wastes, purifying the environment from pollution, being involved in the nitrogen cycle, preventing climate change, etc. [5, 6]. Soil can be directly contaminated by pesticides after their application. The factors that influence presence of chemicals in the soil are water solubility, affinity for pesticides to sorb to organic carbon (K_{oc}), the octanol/water partition coefficient (K_{ow}), and the half-life (DT_{50}) of the chemical in soil [7]. The pesticides degrade in the soil into transformation products (TPs), which can be as toxic as – or even more toxic than – the parent compounds. The degradation occurs through two processes: (1) the chemical process which is performed through photolysis, hydrolysis, oxidation, and reduction reactions; and (2) the microbial process which occurs with the aid of soil microorganisms [8–10].

Pesticides also enter the aquatic ecosystem via various routes such as spray drift, leaching, runoff, etc., and there they cause contamination or affect aquatic organisms [11–13]. Pesticides also find their way into the human digestive system when a person ingests contaminated water or food. Traces of contamination with pesticides were detected in water streams near lands with urban use [7]. Spray drift, volatilization, and aerial application of pesticides also cause contamination of the air by pesticides, which is a possible source of toxicity transmission to many organisms [14]. Another concern due to intensive use of pesticides is pest resistance occurring through the genetic adaptation of pests to specific pesticides due to repeated intensive use thereof, which in turn leads to the ineffectiveness of pesticide application for pest control and the need for higher application doses [15, 16]. Pesticides also jeopardize human health in various ways. The negative chronic health effects associated with pesticide exposure include dermatologic, neurologic, carcinogenic, reproductive, genotoxic, cardiovascular, respiratory, endocrine, immunotoxicity, and gastrointestinal effects [14, 17–19].

There is evidence of long-range transport of persistent pesticides. The chemical properties of CUPs are different from earlier highly persistent pesticides. However, new reports have also shown the presence of many CUPs in remote regions, which is proof of long-range transport of these chemicals. The emergence of CUPs in the Arctic environment in both abiotic and biotic matrices has been reported frequently in papers [20–22]. These findings can be alarming; there are still unknown aspects of the behaviour of CUPs in the environment which make them travel far distances, and consequently attempts to monitor CUPs should not be limited only to specific regions or countries.

Due to the adverse effect of pesticides on human health and the ecosystem, new cultivation strategies have been introduced, such as organic farming (OF), integrated crop management, and integrated pest management (IPM), etc. [14, 23]. The benefits and drawbacks of these methods have proven controversial in the studies and subject to debate [24–27], and they are not considered to be comprehensive methods worldwide. Thus, despite all the advances, it is still crucial to assess pesticide occurrence in different compartments by monitoring them, with the aim of preventing CUPs from accumulating and posing consequent negative effects to the environment.

The term "CUP" is a very general concept and to make it clearer for the reader, it would be necessary to define which compounds were taken into consideration. For preparing this review, except for persistent chlorinated pesticides which have been banned all over the world, we considered as a CUP any pesticide related to other chemical groups. Because there is no unified global regulation regarding the prohibition of compounds, and instead they are mostly under local or national regulations, it is very probable that pesticides banned in many countries have been used in some other countries in recent years. According to the literature, the dawn of soil-monitoring studies for the active ingredients considered CUPs in this chapter was in the USA in 1969 [28]. More representative studies were carried out in the subsequent years on a continent-wide scale like Europe [29, 30] or on the scale of a whole country [31–34]. In Asian countries, representative monitoring studies have been carried out in Korea [35–38] and Saudi Arabia [39], but they are still not sufficient. In the African and American contexts an even lower number of studies have been performed on the monitoring of CUPs over the last 50 years. In this chapter, a review of the studies devoted to the survey and monitoring of CUPs in agricultural soils around the world in the last five-year period, 2016–2020, is presented.

2 Environmental Monitoring and Survey

To evaluate the quality of the environment or the influence of anthropogenic activities on different environmental compartments, environmental-monitoring techniques have been designed. In all monitoring programs, the main goal is providing an early alarm before damage to the environment reaches a critical point [40]. Regular measurement is a crucial part of environmental monitoring. Data from environmental monitoring is used for risk assessment to evaluate the health and environmental impact of pollutants and further for management planning and policy-making. However, there are many situations in which there is no historical record or adequate information on the factors causing the problem. In such cases, surveys are used. Generally, surveys include once-only observation [41, 42].

To record and assess soil changes at an early stage across both time and space, soil variables are determined and investigated. Along with many other factors, soil contamination has also been considered frequently as a threat to soil quality, because soil has the unique property of retaining and degrading contaminants [43–46]. Among all the chemicals and factors causing soil contamination, less attention has been devoted to the residue of pesticides in the soils. As will be clear from this review chapter, there is still a huge need for regular, harmonized, and effective monitoring programs all around the world in order to prevent any irrecoverable damage to this non-renewable resource.

3 Monitoring and Occurrence of CUPs

In total, monitoring data for 280 active ingredients were reported in all reviewed articles. In Table 1 these active ingredients along with their physical-chemical properties are listed. Regarding monitoring CUPs, some countries have been more active in terms of studies published. Moreover, the number of studies published during each year can serve as a helpful indication of the efforts dedicated to soil-monitoring studies by time. So, it would be practical to categorize and present this review of the studies in geographical and chronological order. The sections are arranged according to the continents with the highest number of studies on CUP monitoring in soil in the last 5 years.

3.1 Monitoring and Survey Studies in Europe

Karasali et al. [48] did a study on 66 soil samples of a pilot area including cotton and maize fields in Kopaida, Greece. They were monitored for eight herbicides for 3 years. The main aim was investigating the effectiveness of the Low-Input Crop Management practice in comparison with conventional farms. In total, the most

Table 1 Physical-chemical properties of the active ingredients (parent compounds and TPs) studied in all reviewed articles [47]

No.	Active ingredient	Type	Metabolite	Chemical class	CAS no.	GUS index	Solubility – in water at 20°C (mg/L)	Log *P*	pK_a at 25°C	Vapour pressure at 20°C (mPa)	Henry's law constant at 25°C (Pa/m^3/mol)	Soil DT50 – field (days)	K_{oc} (mL/g)	K_{foc} (mL/g)
1	1-(4-chlorophenyl)-1H-pyrazol-3-ol	Fungicide	Yes	Pyraclostrobin metabolite	–	–	–	–	–	–	–	–	–	–
2	1-[2-chloro-4-(4-chlorophenoxy) phenyl]-2-(1H-1,2,4-triazol-1-yl)ethanol	Fungicide	Yes	Difenoconazole metabolite	–	–	–	–	–	–	–	–	–	–
3	1-[2-chloro-4-(4-chlorophenoxy) phenyl]-2-(1H-1,2,4-triazol-1-yl)ethanone	Fungicide	Yes	Difenoconazole metabolite	–	1.04	12	3.8	–	0.005	–	–	–	2,980
4	1-[3-(p-2-carboxymethylisopropyl)phenyl-2-methylpropyl]piperidine	Fungicide	Yes	Fenpropidin metabolite	–	–	–	–	–	–	–	–	–	–
5	1-[3-(p-2-hydroxymethylisopropyl)phenyl-2-methylpropyl]piperidine	Fungicide	Yes	Fenpropidin metabolite	–	–	–	–	–	–	–	–	–	–
6	1-{[3-(4-tert-butylphenyl)-2-methylpropyl]amino}propan-2-ol	Fungicide	Yes	Fenpropimorph metabolite	–	–	–	–	–	–	–	–	–	–
7	2,4-D	Herbicide	No	Alkylchlorophenoxy	94-75-7	3.82	24,300	−0.82	3.4	0.009	4.00E-06	28.8	39.3	24
8	2,4-dimethylphenyl-N-methylformamidine	–	Yes	–	–	–	–	–	–	–	–	–	–	–
9	2-[(2,6-dimethylphenyl) (methoxy-acetyl)amino] propanoic acid	Fungicide	Yes	Metalaxyl metabolite	–	3.39	265,000	–	–	–	–	17.1	–	17.9
10	2-aminobenzimidazole	Fungicide	Yes	Carbendazim metabolite	–	–	14,900	0.91	–	0.38	–	–	22	–
11	2-ethyl-7-nitro-1-propyl-1H-benzimidazole-5-sulfonamide	Herbicide	Yes	Oryzalin metabolite	–	–	–	–	–	–	–	–	–	–
12	2-ethyl-7-nitro-1-propyl-1H-benzimidazole-5-sulfonamide 3-oxide	Herbicide	Yes	Oryzalin metabolite	–	–	–	–	–	–	–	–	–	–

(continued)

Table 1 (continued)

No.	Active ingredient	Type	Metabolite	Chemical class	CAS no.	GUS index	Solubility – in water at 20°C (mg/L)	Log *P*	pK_a at 25°C	Vapour pressure at 20°C (mPa)	Henry's law constant at 25°C (Pa/m^3/mol)	Soil DT50 – field (days)	K_{oc} (mL/g)	K_{foc} (mL/g)
13	3-(3-chlorophenyl)-1,1-dimethylurea	Herbicide	Yes	Diuron metabolite	–	–	–	–	–	–	–	–	–	–
14	3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)butan-2-one	Fungicide	Yes	Tebuconazole metabolite	–	–	–	–	–	–	–	–	–	–
15	3,5,6-trichloro-2-pyridinol	Insecticide	Yes	Chlorpyrifos metabolite	6515-38-4	3.89	80.9	3.21	–	137.32	1.1	75.3	149	84.5
16	3,5-dibromo-4-hydroxybenzoic acid	Herbicide	Yes	Bromoxynil metabolite	–	−0.41	250,000	–	–	5.20E-03	–	–	–	184
17	3-cyano-2,5,6-trichlorobenzamide	Fungicide	Yes	Chlorothalonil metabolite	–	–	–	–	–	–	–	–	–	–
18	3-cyano-6-hydroxy-2,4,5-trichlorobenzamide / 3-cyano-4-hydroxy-2,5,6-trichlorobenzamide	Fungicide	Yes	Chlorothalonil metabolite	–	–	–	–	–	–	–	–	–	–
19	3-phenoxybenzaldehyde (3-PBA)	Insecticide	Yes	–	–	–	–	–	–	–	–	–	–	–
20	4-cyclopropyl-6-methyl-N-(4-′-hydroxyphenyl)pyrimidine-2-amine	Fungicide	Yes	Cyprodinil metabolite	–	–	–	–	–	–	–	–	–	–
21	4-cyclopropyl-6-methylpyrimidine-2-amine	Fungicide	Yes	Cyprodinil metabolite	–	2.85	–	–	–	–	1.86E-09	148	–	488
22	5-tert-butyl-5-(1H-1,2,4-triazol-1-ylmethyl) dihydrofuran-2(3H)-one	Fungicide	Yes	Tebuconazole metabolite	–	–	–	–	–	–	–	–	–	–
23	Acephate	Insecticide	No	Organophosphate	30560-19-1	1.14	790,000	−0.85	8.35	0.226	5.15E-08	3	302	40.3
24	Acetamiprid	Insecticide	No	Neonicotinoid	135410-20-7	0.94	2,950	0.8	0.7	1.73E-04	5.30E-08	3	200	106.5

25	Acetochlor	Herbicide	No	Chloroacetamide	34256-82-1	1.67	282	4.14	NA	2.20E-02	2.10E-03	12.1	156	285
26	Acetochlor-ESA	Herbicide	Yes	Acetochlor metabolite	–	3.73	–	–	–	–	–	–	28.8	104
27	Acetochlor-OA	Herbicide	Yes	Acetochlor metabolite	500-72-1	2.49	–	–	–	–	–	12	24.3	49.8
28	Acetyl-dinoseb-6-amino	Acaricide	Yes	Dinoseb metabolite	–	–	–	–	–	–	–	–	–	–
29	Alachlor	Herbicide	No	Chloroacetamide	15972-60-8	0.8	240	3.09	0.62	2.9	3.20E-03	14	335	1,994
30	Alachlor-hydroxy	Herbicide	Yes	Alachlor/ acetochlor metabolite	56681-55-1	–	–	1.96	–	–	–	–	278	–
31	AMBA	Herbicide	Yes	Mesotrione metabolite	–	2.65	–	0.32	–	–	–	–	77	52
32	Aminopyralid	Herbicide	No	Pyridine compound	150114-71-9	3.34	2,480	−2.87	2.56	2.59E-09	9.61E-12	21.1	–	8.3
33	AMPA	Herbicide	Yes	Glyphosate metabolite	1066-51-9	0.04	1,466,561	−1.63	–	–	0.16	419	2,002	9,664.5
34	Atrazine	Herbicide	No	Triazine	1912-24-9	2.57	35	2.7	1.7	0.039	1.50E-04	29	100	174
35	Atrazine-2-hydroxy	Herbicide	Yes	Atrazine metabolite	2163-68-0	–	5.9	2.09	–	1.131	6.36E-08	–	–	–
36	Atrazine-desethyl	Herbicide	Yes	Atrazine metabolite	6190-65-4	3.24	2,700	1.51	–	12.44	1.55E-04	45	110	–
37	Atrazine-desethyl-desisopropyl	Herbicide	Yes	Atrazine metabolite	–	–	–	–	–	–	–	–	–	–
38	Atrazine-desisopropyl	Herbicide	Yes	Atrazine metabolite	1007-28-9	–	980	1.15	–	–	980	–	130	–
39	Azoxystrobin	Fungicide	No	Strobilurin	131860-33-8	3.1	6.7	2.5	NA	1.10E-07	7.40E-09	180.7	589	423
40	Azoxystrobin acid	Fungicide	Yes	Azoxystrobin metabolite	–	–	–	–	–	–	–	–	–	–
41	Bentazone	Herbicide	No	Benzothiazinone	25057-89-0	1.95	7,112	−0.46	3.51	0.17	7.20E-05	7.5	55.3	59.6
42	Bifenazate	Insecticide	No	Hydrazine carboxylate	149877-41-8	0.98	2.06	3.4	12.94	1.33E-02	1.01E-03	4.8	1,778	368
43	Bifenox	Herbicide	No	Diphenyl ether	42576-02-3	0.23	0.1	3.64	NA	0.162	1.62E-04	17.3	–	6,475

(continued)

Table 1 (continued)

No.	Active ingredient	Type	Metabolite	Chemical class	CAS no.	GUS index	Solubility – in water at 20°C (mg/L)	Log *P*	pK_a at 25°C	Vapour pressure at 20°C (mPa)	Henry's law constant at 25°C (Pa/m^3/mol)	Soil DT50 – field (days)	K_{oc} (mL/g)	K_{foc} (mL/g)
44	Bifenox-acid	Herbicide	Yes	Bifenox metabolite	53774-07-5	3.23	1,000	4.55	–	–	–	–	–	143
45	Bifenox-amino	Herbicide	Yes	Bifenox metabolite	–	–	–	–	–	–	–	–	–	–
46	Bifenthrin	Insecticide	No	Pyrethroid	82657-04-3	−2.66	0.001	6.6	NA	0.0178	7.74E-05	86.8	236,610	–
47	Bitertanol	Fungicide	No	Triazole	55179-31-2	0.83	3.8	4.1	NA	1.36E-06	2.60E-07	23	–	2,461
48	Bitertanol benzoic acid	Fungicide	Yes	Bitertanol metabolite	–	–	–	–	–	–	0.16	–	–	–
49	Bitertanol ketone	Fungicide	Yes	Bitertanol metabolite	–	–	–	–	–	–	–	–	–	–
50	Boscalid	Fungicide	No	Carboxamide	188425-85-6	2.68	4.6	2.96	NA	0.00072	5.18E-05	254	–	772
51	Bromoxynil	Herbicide	No	Hydroxybenzonitrile	1689-84-5	1.71	38,000	0.27	3.86	0.12	8.70E-07	8	302	127.2
52	Bupirimate	Fungicide	No	Pyrimidinol	41483-43-6	1.11	13.06	3.68	4.4	0.057	1.35	34	–	1,882
53	Buprofezin	Insecticide	No	Unclassified	69327-76-0	0.45	0.46	4.93	NA	0.042	2.80E-02	45.6	5,363	5,334
54	Butachlor	Herbicide	No	Chloroacetamide	23184-66-9	1.23	20	4.5	–	0.24	3.74E-03	11.5	700	–
55	Cadusafos	Insecticide	No	Organophosphate	95465-99-9	2.62	245	3.85	NA	119.6	0.132	39	–	227
56	Carbaryl	Insecticide	No	Carbamate	63-25-2	2.02	9.1	2.36	10.4	0.0416	9.20E-05	–	300	211
57	Carbendazim	Fungicide	No	Benzimidazole	10605-21-7	2.21	8	1.48	4.2	0.09	3.60E-03	22	–	225
58	Carbetamide	Herbicide	No	Carbamate	16118-49-3	1.85	3,270	1.78	11.3	0.0003	1.93E-08	8	–	88.6
59	Carbofuran	Insecticide	No	Carbamate	1563-66-2	2.36	322	1.8	NA	0.08	5.00E-05	14	–	86.5

60	Chlorantraniliprole	Insecticide	No	Anthranilic diamide	500008-45-7	3.51	0.88	2.86	10.88	6.30E-09	3.20E-09	204	362	301
61	Chlorfenapyr	Insecticide	No	Pyrrole	122453-73-0	−0.01	0.112	4.83	NA	9.81E-03	5.81E-04	–	12,000	–
62	Chlorfenvinphos	Insecticide	No	Organophosphate	470-90-6	1.72	145	3.8	–	0.53	–	30	680	–
63	Chloridazon	Herbicide	No	Pyridazinone	1698-60-8	2.16	422	1.19	3.38	1.00E-06	5.30E-10	34.7	120	199
64	Chloridazon-methyl-desphenyl	Herbicide	Yes	Chloridazon metabolite	–	4.39	–	−1.38	–	–	–	–	–	92
65	Chlorothalonil	Fungicide	No	Chloronitrile	1897-45-6	1.12	0.81	2.94	NA	0.076	2.50E-02	17.9	2,632	1,288
66	Chlorothalonil-4-hydroxy	Fungicide	Yes	Chlorothalonil metabolite	–	2.56	13.5	0.61	–	–	–	–	498	383
67	Chlorotoluron	Herbicide	No	Urea	15545-48-9	–	74	2.5	NA	0.005	1.44E-05	34	196	–
68	Chlorotoluron-desmethyl	Herbicide	Yes	Chlorotoluron metabolite	–	2.84	–	–	–	–	1.09E-03	–	248	–
69	Chlorotoluron-didesmethyl	Herbicide	Yes	Chlorotoluron metabolite	–	–	–	–	–	–	–	–	–	–
70	Chlorpyrifos	Insecticide	No	Organophosphate	2921-88-2	0.58	1.05	4.7	NA	1.43	0.478	27.6	5,509	3,954
71	Chlorsulfuron	Herbicide	No	Sulfonylurea	64902-72-3	3.8	12,500	−0.99	3.4	3.07E-06	3.50E-11	36.2	–	36.3
72	Clomazone	Herbicide	No	Isoxazolidinone	81777-89-1	2.72	1,212	2.58	NA	27	5.90E-03	27.3	300	128.3
73	Clopyralid	Herbicide	No	Pyridine compound	1702-17-6	3.02	7,850	−2.63	2.01	1.36E-09	1.80E-11	8.2	5	–
74	CMBA	Herbicide	Yes	Sulcotrione metabolite	53250-83-2	–	60,000	−0.2	–	–	–	8.5	–	4.76
75	Cyanophenoxy pyrimidinol	Fungicide	Yes	Azoxystrobin metabolite	–	–	–	–	–	–	–	–	–	–
76	Cyfluthrin	Insecticide	No	Pyrethroid	68359-37-5	−1.66	0.0066	6	NA	0.0003	5.30E-02	33	123,930	–
77	Cyhalothrin	Insecticide	No	Pyrethroid	68085-85-8	−2.2	0.004	6.8	9	1.00E-09	1.80E-02	–	180,000	–
78	Cyhalothrin-λ	Insecticide	No	Pyrethroid	91465-08-6	−2.09	0.005	5.5	NA	0.0002	2.00E-02	26.9	283,707	290,311

(continued)

Table 1 (continued)

No.	Active ingredient	Type	Metabolite	Chemical class	CAS no.	GUS index	Solubility – in water at 20°C (mg/L)	Log *P*	pK_a at 25°C	Vapour pressure at 20°C (mPa)	Henry's law constant at 25°C (Pa/m^3/mol)	Soil DT50 – field (days)	K_{oc} (mL/g)	K_{foc} (mL/g)
79	Cymoxanil	Fungicide	No	Cyanoacetamide oxime	57966-95-7	1.47	780	0.67	9.3	0.15	3.80E-05	3.5	–	43.6
80	Cypermethrin	Insecticide	No	Pyrethroid	52315-07-8	−1.99	0.009	5.55	NA	6.78E-03	0.31	21.9	307,558	–
81	Cypermethrin-α	Insecticide	No	Pyrethroid	67375-30-8	−2.38	0.004	5.8	NA	0.00038	5.30E-02	42.6	288,735	–
82	Cyproconazole	Fungicide	No	Triazole	94361-06-5	3.04	93	3.09	NA	0.026	5.00E-05	129	–	364
83	Cyprodinil	Fungicide	No	Anilinopyrimidine	121552-61-2	1.06	13	4	4.44	5.10E-01	6.60E-03	45	–	2,277
84	Deltamethrin	Insecticide	No	Pyrethroid	52918-63-5	−3.98	0.0002	4.6	NA	1.2E-05	3.10E-02	21	1E+07	1E+07
85	Desmedipham	Herbicide	No	Carbamate	13684-56-5	0.35	5.6	2.7	NA	4.00E-05	5.40E-07	8	–	4,124
86	Diazinon	Insecticide	No	Organophosphate	333-41-5	1.51	60	3.69	2.6	11.97	6.09E-02	18.4	609	643
87	Dicamba	Herbicide	No	Benzoic acid	1918-00-9	1.72	250,000	−1.88	1.87	1.67	1.00E-04	3.9	–	12.36
88	Dichlorvos	Insecticide	No	Organophosphate	62-73-7	0.69	18,000	1.9	NA	2,100	2.58E-02	–	50	–
89	Difenoconazole	Fungicide	No	Triazole	119446-68-3	0.83	15	4.36	1.07	3.33E-05	9.00E-07	85	–	3,760
90	Diflubenzuron	Insecticide	No	Benzoylurea	35367-38-5	0.17	0.08	3.89	–	0.00012	4.70E-04	–	–	4,620
91	Diflufenican	Herbicide	No	Carboxamide	83164-33-4	1.19	0.05	4.2	–	4.25E-03	1.18E-02	64.6	5,504	2,215
92	Dimethachlor	Herbicide	No	Chloroacetamide	50563-36-5	1.09	2,300	2.17	NA	0.64	1.70E-04	3.2	–	69
93	Dimethachlor-ESA	Herbicide	Yes	Dimethachlor metabolite	–	4.05	–	–	–	–	–	Soil, groundwater	–	–

94	Dimethachlor-hydroxy	Herbicide	Yes	Dimethachlor metabolite	–	–	–	–	–	–	–	–	–	–
95	Dimethachlor-OA	Herbicide	Yes	Dimethachlor metabolite	–	8.5	–	–	–	–	–	Soil, groundwater	–	–
96	Dimethenamid	Herbicide	No	Chloroacetamide	87674-68-8	2.41	1,200	2.2	NA	0.37	8.60E-03	13	–	69
97	Dimethenamid-ESA	Herbicide	Yes	Dimethenamid metabolite	–	5.52	–	–	–	–	–	57	6.7	7.18
98	Dimethenamid-OA	Herbicide	Yes	Dimethenamid metabolite	–	5.4	–	–	–	–	–	69	7.7	11.6
99	Dimethenamid-P	Herbicide	No	Chloroacetamide	163515-14-8	1.97	1,499	1.89	NA	2.51	4.80E-04	7	–	227
100	Dimethoate	Insecticide	No	Organophosphate	60-51-5	2.18	25,900	0.75	NA	0.247	1.42E-06	7.2	–	28.3
101	Dimethomorph	Fungicide	No	Morpholine	110488-70-5	2.26	28.95	2.68	−1.3	9.70E-04	2.50E-05	44	–	419.4
102	Dimethomorph (3or 4) demethyl	Fungicide	Yes	Dimethomorph metabolite	–	–	–	–	–	–	–	–	–	–
103	Dimethylvinphos	Insecticide	No	Organophosphate	2274-67-1	2.44	130	3.13	NA	1.3	–	–	300	–
104	Dimoxystrobin	Fungicide	No	Strobilurin	149961-52-4	1.79	4.3	3.59	NA	6.00E-06	4.55E-08	22.9	–	486
105	Dinoseb	Herbicide	No	Dinitrophenol	88-85-7	3.73	52	2.29	4.62	6.7	6.01E-04	–	30	–
106	Dinoseb-6-amino	Acaricide	Yes	Dinoseb metabolite	–	–	–	–	–	–	–	–	–	–
107	Diuron	Herbicide	No	Phenylamide	330-54-1	2.65	35.6	2.87	NA	1.15E-03	2.00E-06	229	680	757
108	Diuron-desdimethyl	Herbicide	Yes	Diuron/linuron metabolite	2327-02-8	1.03	940	2.35	–	–	–	–	695	694
109	Diuron-desmonomethyl	Herbicide	Yes	Diuron/linuron metabolite	3567-62-2	2.17	490	–	–	–	–	–	–	928
110	Emamectin	–	No	–	–	–	–	–	–	–	–	–	–	–
111	Epoxiconazole	Fungicide	No	Triazole	135319-73-2	2.09	7.1	3.3	NA	1.00E-02	4.71E-04	120	–	1,073
112	Esfenvalerate	Insecticide	No	Pyrethroid	66230-04-4	−1.8	0.001	6.24	NA	1.17E-09	4.92E-04	19.2	251,717	–
113	Ethalfluralin	Herbicide	No	Dinitroaniline	55283-68-6	0.47	0.01	5.11	NA	12	18	53	6,364	5,356

(continued)

Table 1 (continued)

No.	Active ingredient	Type	Metabolite	Chemical class	CAS no.	GUS index	Solubility – in water at 20°C (mg/L)	Log P	pK_a at 25°C	Vapour pressure at 20°C (mPa)	Henry's law constant at 25°C (Pa/m^3/mol)	Soil DT50 – field (days)	K_{oc} (mL/g)	K_{foc} (mL/g)
114	Ethirimol	Fungicide	No	Pyrimidinol	23947-60-6	1.82	233	2.3	5	0.267	2.00E-04	20	–	402
115	Ethofumesate	Herbicide	No	Benzofuran	26225-79-6	3.04	50	2.7	NA	0.36	3.72E-03	37.8	–	118
116	Fenarimol	Fungicide	No	Pyrimidine	60168-88-9	2.12	13.7	3.69	–	0.065	7.00E-04	74	–	734
117	Fenazaquin	Insecticide	No	Quinazoline	120928-09-8	−0.63	0.102	5.51	2.44	1.90E-02	5.71E-02	30.5	–	26,499
118	Fenitrothion	Insecticide	No	Organophosphate	122-14-5	0.48	19	3.32	NA	0.676	9.86E-03	–	2000	791
119	Fenpropathrin	Insecticide	No	Pyrethroid	39515-41-8	−0.8	0.33	6.04	–	0.76	#######	28	5,000	35,660
120	Fenpropidin	Fungicide	No	Unclassified	67306-00-7	0.71	530	2.6	10.13	17	10.7	49.2	–	3,808
121	Fenpropidin-hydroxy	Fungicide	Yes	Fenpropidin metabolite	–	–	–	–	–	–	–	–	–	–
122	Fenpropidin-N-oxide	Fungicide	Yes	Fenpropidin metabolite	–	–	–	–	–	–	–	–	–	–
123	Fenpropimorph	Fungicide	No	Morpholine	67564-91-4	0.5	4.32	4.5	6.98	3.9	2.74E-04	25.5	–	4,382
124	Fenpropimorph carboxy	Fungicide	Yes	Fenpropimorph metabolite	–	–	–	–	–	–	–	–	–	–
125	Fenpyroximate	Insecticide	No	Pyrazolium	134098-61-6	0.26	0.023	5.01	NA	0.01	0.182	4.3	–	52,067
126	Fenthion	Insecticide	No	Organophosphate	55-38-9	1.26	4.2	4.84	–	0.37	2.40E-02	–	1,500	–
127	Fenvalerate	Insecticide	No	Pyrethroid	51630-58-1	0.52	0.001	5.01	–	0.0192	4.20E-02	–	5,273	–
128	Florasulam	Herbicide	No	Triazolopyrimidine	145701-23-1	2.5	6,360	−1.22	4.54	0.01	4.35E-07	8.5	22	20.37
129	Fluazifop-P-acid	Herbicide	Yes	Fluazifop-p-butyl metabolite	83066-88-0	3.23	40.5	3.18	3.12	–	–	–	205	48.72

130	Fluazifop-P-butyl	Herbicide	No	Aryloxyphenoxypropionate	79241-46-6	0.43	0.93	4.5	NA	0.12	0.049	8.2	3,394	–
131	Fluazinam	Fungicide	No	Phenylpyridinamine	79622-59-6	1	0.135	4.03	7.34	7.5	25.9	16.4	16,430	1958
132	Fluazinam-3-hydroxy	Fungicide	Yes	Fluazinam metabolite	–	–	–	–	–	–	–	–	–	–
133	Fludioxonil	Fungicide	No	Phenylpyrrole	131341-86-1	−1.35	1.8	4.12	0	3.90E-04	5.40E-05	20.5	145,600	132,100
134	Flumequine	–	No	–	–	–	–	–	–	–	–	–	–	–
135	Fluometuron	Herbicide	No	Phenylurea	2164-17-2	4.24	111	2.28	NA	0.125	2.63E-04	89.8	–	67.4
136	Fluroxypyr	Herbicide	No	Pyridine compound	69377-81-7	1.03	6,500	0.04	2.94	3.8E-06	1.69E-10	51	–	68
137	Flusilazole	Fungicide	No	Triazole	85509-19-9	1.54	41.9	3.87	2.5	0.0387	2.70E-04	94	1,664	–
138	Folpet	Fungicide	No	Phthalimide	133-07-3	0.72	0.8	3.02	NA	2.10E-02	8.00E-03	3	304	–
139	Glyphosate	Herbicide	No	Organophosphate	1071-83-6	−0.29	10,500	−3.2	2.34	0.0131	2.10E-07	23.79	1,424	16,331
140	Hexaconazole	Fungicide	No	Triazole	79983-71-4	2.31	18	3.9	2.3	0.018	3.33E-04	225	1,040	–
141	Hexythiazox	Insecticide	No	Carboxamide	78587-05-0	0.03	0.1	2.67	NA	1.33E-03	1.19E-02	17.7	–	9,455
142	Imazalil	Fungicide	No	Imidazole	35554-44-0	0.26	184	2.56	6.49	0.158	0.00011	6.4	–	4,753
143	Imidacloprid	Insecticide	No	Neonicotinoid	138261-41-3	3.69	610	0.57	NA	4.00E-07	1.70E-10	174	–	225
144	Imidacloprid-guanidine	Insecticide	Yes	Imidacloprid metabolite	–	–	–	–	–	–	–	–	–	–
145	Imidacloprid-urea	Insecticide	Yes	Imidacloprid metabolite	–	–	–	–	–	–	–	–	–	–
146	Indoxacarb	Insecticide	No	Oxadiazine	173584-44-6	0.27	0.2	4.65	NA	9.80E-06	6.00E-05	5.97	4,483	–
147	Ioxynil	Herbicide	No	Hydroxybenzonitrile	1689-83-4	1.06	3,034	2.2	4.1	0.00204	1.50E-05	5	–	303

(continued)

Table 1 (continued)

No.	Active ingredient	Type	Metabolite	Chemical class	CAS no.	GUS index	Solubility – in water at 20°C (mg/L)	Log *P*	pK_a at 25°C	Vapour pressure at 20°C (mPa)	Henry's law constant at 25°C (Pa/m^3/mol)	Soil DT50 – field (days)	K_{oc} (mL/g)	K_{foc} (mL/g)
148	Iprodione	Fungicide	No	Dicarboximide	36734-19-7	0.43	6.8	3	NA	0.0005	7.00E-06	11.7	700	3,927
149	Isocarbophos	Insecticide	No	Organophosphate	24353-61-5	–	70.1	2.7	–	–	–	–	190	–
150	Isoproturon	Herbicide	No	Urea	34123-59-6	2.61	70.2	2.5	NA	5.50E-03	1.46E-05	23	–	122
151	Isoproturon-didemethyl	Herbicide	Yes	Isoproturon metabolite	–	–	–	–	–	–	–	–	–	–
152	Isoproturon-monodemethyl	Herbicide	Yes	Isoproturon metabolite	34123-57-4	2.78	–	–	–	–	–	–	–	147
153	Kresoxim-methyl	Fungicide	No	Strobilurin	143390-89-0	0	2	3.4	NA	2.30E-03	3.60E-04	–	–	308
154	Lactofen	Herbicide	No	Diphenyl ether	77501-63-4	0	0.5	–	–	0.0093	4.56E-03	–	10,000	–
155	Lenacil	Herbicide	No	Uracil	2164-08-1	3.02	2.9	1.69	10.7	1.70E-06	1.30E-07	39.8	165	130
156	Lenacil-oxo	Herbicide	Yes	Lenacil metabolite	–	–	–	–	–	–	–	–	–	–
157	Linuron	Herbicide	No	Urea	330-55-2	2.11	63.8	3	NA	0.051	2.00E-04	48	842.8	559
158	Linuron-desmethyl	Herbicide	Yes	Linuron metabolite	–	–	–	–	–	–	–	–	–	–
159	Lufenuron	Insecticide	No	Benzoylurea	103055-07-8	−1.48	0.046	5.12	10.2	4.00E-03	3.41E-02	256	–	41,182
160	Maneb	Fungicide	No	Carbamate	12427-38-2	0.75	178	−0.45	NA	0.014	2.08E-05	7	2000	1,310
161	MCPA	Herbicide	No	Aryloxyalkanoic acid	94-74-6	2.98	29,390	−0.81	3.73	0.4	5.50E-05	25	–	74
162	MCPA (methyl ester)	Herbicide	No	Aryloxyalkanoic acid	–	–	–	–	–	–	–	–	–	–
163	Mecoprop	Herbicide	No	Aryloxyalkanoic acid	7085-19-0	2.29	250,000	−0.19	3.11	1.6	2.20E-04	–	47	31
164	Mecoprop-P	Herbicide	No	Aryloxyalkanoic acid	16484-77-8	2.94	250,000	−0.19	3.7	0.23	5.70E-05	21	–	59.8

165	Mesotrione	Herbicide	No	Triketone	104206-82-8	1.45	1,500	0.11	3.12	5.70E-03	5.10E-07	5	122	83.3
166	Metalaxyl	Fungicide	No	Phenylamide	57837-19-1	2.06	8,400	1.75	0	0.75	1.60E-05	38.7	162	162.3
167	Metalaxyl-M	Fungicide	No	Phenylamide	70630-17-0	2.42	26,000	1.71	NA	3.3	3.50E-05	14.1	–	78.9
168	Metamitron	Herbicide	No	Triazinone	41394-05-2	2.16	1770	0.85	NA	7.44E-04	8.95E-08	11.1	77.7	86.4
169	Metamitron-desamino	Herbicide	Yes	Metamitron metabolite	–	2.97	399.9	–	–	–	–	31.1	–	103
170	Metazachlor	Herbicide	No	Chloroacetamide	67129-08-2	1.75	450	2.49	NA	0.093	5.90E-05	6.8	54	79.6
171	Metazachlor-deschloro	Herbicide	Yes	Metazachlor metabolite	–	–	–	–	–	–	–	–	–	–
172	Metazachlor-ESA	Herbicide	Yes	Metazachlor metabolite	–	6.8	–	–	–	–	–	115	8.8	5
173	Metazachlor-hydroxy	Herbicide	Yes	Metazachlor metabolite	–	–	–	–	–	–	–	–	–	–
174	Metazachlor-OA	Herbicide	Yes	Metazachlor metabolite	–	5.18	–	–	–	–	–	96.3	18.9	24.6
175	Metconazole	Fungicide	No	Triazole	125116-23-6	2.03	30.4	3.85	11.38	2.10E-05	2.21E-07	134.7	–	1,116
176	Methamidophos	Insecticide	No	Organophosphate	10265-92-6	2.41	200,000	−0.79	–	2.3	1.60E-06	4	1	–
177	Methoxyfenozide	Insecticide	No	Diacylhydrazine	161050-58-4	3	3.3	3.72	12.2	1.33E-02	1.64E-04	68	402	231
178	Methyl-N-(3-hydroxyphenyl) carbamate	Herbicide	Yes	Phenmedipham metabolite	13683-89-1	1.62	–	1.3	–	–	–	–	–	48
179	Metolachlor	Herbicide	No	Chloroacetamide	51218-45-2	2.36	530	3.4	NA	1.7	2.40E-03	21	120	163
180	Metolachlor-demethyl	Herbicide	Yes	Metolachlor metabolite	–	–	–	–	–	–	–	–	–	–
181	Metolachlor-ESA	Herbicide	Yes	Metolachlor metabolite	171118-09-5	7.22	212,461	−1.89	–	–	–	–	9	–
182	Metolachlor-OA	Herbicide	Yes	Metolachlor metabolite	152019-73-3	6.88	238	–	–	–	–	127.5	17	7.26
183	Metribuzin	Herbicide	No	Triazinone	21087-64-9	2.96	10,700	1.75	1.3	0.121	2.50E-05	19	–	37.92
184	Metribuzin-desamino	Herbicide	Yes	Metribuzin metabolite	–	1.25	475	–	–	6.50E-03	–	–	–	43.7

(continued)

Table 1 (continued)

No.	Active ingredient	Type	Metabolite	Chemical class	CAS no.	GUS index	Solubility – in water at 20°C (mg/L)	Log *P*	pK_a at 25°C	Vapour pressure at 20°C (mPa)	Henry's law constant at 25°C (Pa/m^3/mol)	Soil DT50 – field (days)	K_{oc} (mL/g)	K_{foc} (mL/g)
185	Metribuzin-diketo	Herbicide	Yes	Metribuzin metabolite	56507-37-0	3.61	3,300	0.9	–	0.081	–	–	99	48
186	Mevinphos	Insecticide	No	Organophosphate	7786-34-7	1.12	600,000	0.127	–	17	6.30E-06	–	44	–
187	MNBA	Herbicide	Yes	Mesotrione metabolite	110964-79-9	1.86	–	−1.3	–	–	–	–	6	3.2
188	Monocrotophos	Insecticide	No	Organophosphate	6923-22-4	4.02	818,000	−0.22	–	0.29	–	30	19	–
189	Myclobutanil	Fungicide	No	Triazole	88671-89-0	1.99	132	2.89	2.3	0.198	4.33E-04	35	–	517
190	N-(2,6-dimethylphenyl)-N-(methoxyacetyl)alanine	Fungicide	Yes	Metalaxyl metabolite	–	4.38	–	–	–	–	4.54	51	38	27.2
191	Napropamid	Herbicide	No	Alkanamide	15299-99-7	1.96	74	3.3	NA	2.20E-02	8.10E-05	72	839	885
192	Napropamide-didesethyl	Herbicide	Yes	Napropamide metabolite	–	–	–	–	–	–	–	–	–	–
193	Nicosulfuron	Herbicide	No	Sulfonylurea	111991-09-4	3.44	7,500	0.61	4.78	8.00E-07	1.48E-11	19.3	30	21
194	N-propyl-N-(2-(2,4,6-trichlorophenoxy)ethyl)urea	Fungicide	Yes	Prochloraz metabolite	–	–	–	–	–	–	–	–	–	–
195	N-propyl-N-2-(2,4,6-trichlorophenoxy)-ethylamine	Fungicide	Yes	Prochloraz metabolite	–	–	–	–	–	–	–	–	–	–
196	Omethoate	Insecticide	No	Organophosphate	1113-02-6	2.73	500,000	−0.9	–	19	4.62E-09	14	41.3	–
197	Orbencarb	Herbicide	No	Thiocarbamate	34622-58-7	–	24	4.17	–	4.26	1.33E-01	–	–	–
198	Orbencarb-desethyl	Herbicide	Yes	Orbencarb metabolite	–	–	–	–	–	–	–	–	–	–
199	Oryzalin	Herbicide	No	Dinitroaniline	19044-88-3	2.27	1.13	3.73	9.4	1.10E-07	3.37E-08	98.2	949	724

200	Oryzalin-despropyl	Herbicide	Yes	Oryzalin metabolite	–	–	–	–	–	–	–	–	–	–
201	Oxyfluorfen	Herbicide	No	Diphenyl ether	42874-03-3	0.23	0.116	4.86	NA	0.026	0.02382	73	–	7,566
202	Parathion-ethyl	Insecticide	No	Organophosphate	56-38-2	1.52	12.4	3.83	–	0.89	3.02E-02	17	7,660	580
203	Parathion-methyl	Insecticide	No	Organophosphate	298-00-0	1.35	55	3	–	0.2	8.57E-03	10	240	442
204	Penconazole	Fungicide	No	Triazole	66246-88-6	1.28	73	3.72	1.51	0.366	6.60E-04	90	–	2,205
205	Pendimethalin	Herbicide	No	Dinitroaniline	40487-42-1	−0.28	0.33	5.4	2.8	3.34	1.27	100.6	17,491	13,792
206	Pendimethalin-benzimidazol	Herbicide	Yes	Pendimethalin metabolite	–	–	–	–	–	–	–	–	–	–
207	Permethrin	Insecticide	No	Pyrethroid	52645-53-1	−1.62	0.2	6.1	–	0.007	1.89E-01	42	100,000	–
208	Pethoxamid	Herbicide	No	Chloroacetamide	106700-29-2	1.96	400	2.96	NA	2.8	1.18E-03	14.8	–	211
209	Phenmedipham	Herbicide	No	Carbamate	13684-63-4	1.15	1.8	2.7	NA	7.00E-07	2.70E-08	16.7	1,775	1,142
210	Phorate	Insecticide	No	Organophosphate	298-02-2	1.4	50	3.86	–	112	5.90E-01	63	1,660	–
211	Phosalone	Insecticide	No	Organophosphate	2310-17-0	0.21	1.4	4.01	–	1.56E-02	2.04E-03	–	2063	–
212	Phosmet	Insecticide	No	Organophosphate	732-11-6	0.48	15.2	2.8	NA	0.065	1.36E-03	9.6	3,534	3,212
213	Phthalimide	Fungicide	Yes	Folpet metabolite	85-41-6	0.61	360	1.15	8.3	1.33E-03	1.10E-03	–	209	–
214	Picloram	Herbicide	No	Pyridine compound	1918-02-1	4.8	560	−1.92	2.3	8.00E-05	3.00E-07	36	13	7.22
215	Picoxystrobin	Fungicide	No	Strobilurin	117428-22-5	1.35	3.1	3.6	NA	0.0055	6.00E-04	19.3	965	898
216	Pirimicarb	Insecticide	No	Carbamate	23103-98-2	1.35	3,100	1.7	4.4	0.43	3.30E-05	9	–	388
217	Pirimicarb-desmethyl	Insecticide	Yes	Pirimicarb metabolite	–	–	–	–	–	–	–	–	–	–
218	Prochloraz	Fungicide	No	Imidazole	67747-09-5	1.55	26.5	3.5	3.8	0.15	1.64E-03	16.7	500	1,440

(continued)

Table 1 (continued)

No.	Active ingredient	Type	Metabolite	Chemical class	CAS no.	GUS index	Solubility – in water at 20°C (mg/L)	Log P	pK_a at 25°C	Vapour pressure at 20°C (mPa)	Henry's law constant at 25°C (Pa/m^3/mol)	Soil DT50 – field (days)	K_{oc} (mL/g)	K_{foc} (mL/g)
219	Procymidone	Fungicide	No	Dicarboximide	32809-16-8	3.3	2.46	3.3	NA	0.023	2.65E-03	208.3	378	–
220	Profenofos	Insecticide	No	Organophosphate	41198-08-7	0.59	28	1.7	NA	2.53	1.65E-03	7	2,016	–
221	Prometryn	Herbicide	No	Triazine	7287-19-6	0.59	33	3.34	4.1	0.13	1.20E-03	–	400	4,330
222	Propachlor	Herbicide	No	Chloroacetamide	1918-16-7	1.47	580	1.6	–	30.6	3.65E-03	–	80	–
223	Propachlor-ESA	Herbicide	Yes	Propachlor metabolite	–	–	–	–	–	–	–	–	–	–
224	Propachlor-OA	Herbicide	Yes	Propachlor metabolite	–	–	–	–	–	–	–	–	–	–
225	Propamocarb	Fungicide	No	Carbamate	24579-73-5	–	900,000	0.84	9.5	730	1.50E-04	–	–	–
226	Propaquizafop	Herbicide	No	Aryloxyphenoxypropionate	111479-05-1	2.67	0.63	4.78	NA	4.39E-07	9.20E-08	85	–	–
227	Propiconazole	Fungicide	No	Triazole	60207-90-1	1.58	150	3.72	1.09	0.056	9.20E-05	35.2	1,086	955
228	Propoxur	Insecticide	No	Carbamate	114-26-1	3.65	1800	0.14	–	1.3	1.50E-04	28	30	–
229	Prosulfocarb	Herbicide	No	Thiocarbamate	52888-80-9	0.76	13.2	4.48	NA	0.79	0.0152	9.8	–	1,693
230	Prothioconazole	Fungicide	No	Triazolinthione	178928-70-6	−0.07	22.5	2	6.9	7.40E-06	1.10E-08	0.77	1,765	2,556
231	Pyraclostrobin	Fungicide	No	Strobilurin	175013-18-0	0.05	1.9	3.99	NA	2.60E-05	5.31E-06	33.3	9,304	9,315
232	Pyridaben	Insecticide	No	Pyridazinone	96489-71-3	−1.2	0.022	6.37	NA	0.001	0.3	29	–	66,503
233	Pyrifenox	Fungicide	No	Pyridine	88283-41-4	1.84	300	3.4	4.61	1.7	5.80E-03	66	980	–

234	Pyrimethanil	Fungicide	No	Anilinopyrimidine	53112-28-0	2.17	110	2.84	3.52	1.1	2.20E-03	31.4	–	355.7
235	Quinalphos	Insecticide	No	Organophosphate	13593-03-8	1.1	17.8	4.44	–	0.346	4.70E-03	–	1,465	–
236	Quinmerac	Herbicide	No	Quinoline	90717-03-6	2.05	107,000	−1.41	4.31	1.00E-07	1.00E-10	9.8	86	86
237	Quinoxyfen	Fungicide	No	Quinoline	124495-18-7	−0.8	0.047	5.1	NA	0.012	3.08E-02	169.3	–	22,929
238	Quizalofop-P-ethyl	Herbicide	No	Aryloxyphenoxypropionate	100646-51-3	0.19	0.61	4.61	NA	1.10E-04	6.70E-05	1.8	–	1,816
239	Resmethrin	Insecticide	No	Pyrethroid	10453-86-8	−1.48	0.01	5.43	–	0.0015	8.93E-02	–	100,000	–
240	Simazine	Herbicide	No	Triazine	122-34-9	2.2	5	2.3	1.62	0.00081	5.60E-05	90	130	750
241	Simazine-2-hydroxy	Herbicide	Yes	Simazine metabolite	2599-11-3	–	32.8	1.67	–	–	–	–	5	–
242	S-metolachlor	Herbicide	No	Chloroacetamide	87392-12-9	2.32	480	3.05	NA	3.7	2.20E-03	21	–	226.1
243	S-metolachlor-ESA	Herbicide	Yes	S-metolachlor metabolite	–	–	–	–	–	–	–	–	–	–
244	S-metolachlor-OA	Herbicide	Yes	S-metolachlor metabolite	–	–	–	–	–	–	–	–	–	–
245	Spinosad	Insecticide	No	Micro-organism derived	168316-95-8	–	–	–	–	–	–	–	–	–
246	Spirodiclofen	Insecticide	No	Tetronic acid	148477-71-8	−0.42	0.05	5.83	–	3.00E-04	2.00E-02	–	31,037	–
247	Spiroxamine	Fungicide	No	Morpholine	118134-30-8	−0.28	405	2.89	6.9	3.5	3.80E-03	57.5	–	14,567
248	Spiroxamine acid	Fungicide	Yes	Spiroxamine metabolite	–	–	–	–	–	–	–	–	–	–
249	Spiroxamine desethyl acid	Fungicide	Yes	Spiroxamine metabolite	–	–	–	–	–	–	–	–	–	–
250	Spiroxamine-desethyl	Fungicide	Yes	Spiroxamine metabolite	–	0.49	14.8	–	–	–	–	–	–	4,816
251	Spiroxamine-despropyl	Fungicide	Yes	Spiroxamine metabolite	–	0.58	46.6	–	–	–	–	–	–	4,165
252	Sulcotrione	Herbicide	No	Triketone	99105-77-8	1.36	165	−1.7	3.13	5.00E-03	6.00E-07	3.6	–	36

(continued)

Table 1 (continued)

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253	Tebuconazole	Fungicide	No	Triazole	107534-96-3	1.86	36	3.7	5	1.30E-03	1.00E-05	47.1	–	769
254	Tebuconazole-4-hydroxy	Fungicide	Yes	Tebuconazole metabolite	–	–	–	–	–	–	–	–	–	–
255	Tebuconazole-5-enol or 5-keto	Fungicide	Yes	Tebuconazole metabolite	–	–	–	–	–	–	–	–	–	–
256	Tebufenozide	Insecticide	No	Diacylhydrazine	112410-23-8	1.72	0.83	4.25	NA	1.56E-04	6.59E-05	24.2	–	572
257	Tebufenozide-phenylacetic acid	Insecticide	Yes	Tebufenozide metabolite	–	1.11	10.39	–	–	–	–	–	–	78
258	Tebutam	Herbicide	No	Benzamide	35256-85-0	4.63	790	3	–	89	1.50E-02	–	25	–
259	Teflubenzuron	Insecticide	No	Benzoylurea	83121-18-0	−0.47	0.01	4.3	9.2	9.16E-04	6.98E-03	13.7	26,062	–
260	Terbuthylazine	Herbicide	No	Triazine	5915-41-3	2.19	6.6	3.4	1.9	0.152	2.30E-03	21.8	–	231
261	Terbuthylazine-2-hydroxy	Herbicide	Yes	Terbuthylazine metabolite	–	4.75	7.19	–	–	7.60E-04	–	–	–	187
262	Terbuthylazine-desethyl	Herbicide	Yes	Terbuthylazine metabolite	–	3.07	327.1	2.3	–	0.35	–	28.6	–	78
263	Terbuthylazine-desethyl-2-hydroxy	Herbicide	Yes	Terbuthylazine metabolite	–	–	–	–	–	–	–	–	257	195
264	Terbutryn	Herbicide	No	Triazine	886-50-0	2.21	25	3.66	4.3	0.13	1.50E-03	52	2,432	518
265	Tetramethrin	Insecticide	No	Pyrethroid	7696-12-0	−0.42	1.83	4.6	–	2.1	1.71E-01	–	1,423	–
266	T-fluvalinate	Insecticide	No	Pyrethroid	102851-06-9	−0.69	0.00103	7.02	NA	9.00E-08	1.20E-04	3.51	135,000	186,000
267	Thiacloprid	Insecticide	No	Neonicotinoid	111988-49-9	1.1	184	1.26	NA	3.00E-07	4.80E-10	8.1	–	615
268	Thiacloprid amide	Insecticide	Yes	Thiacloprid metabolite	–	3.35	660	–	–	3.40E-07	–	128	–	258
269	Thiacloprid diamide	Insecticide	Yes	Thiacloprid metabolite	–	–	–	–	–	–	–	–	–	–

270	Thiamethoxam	Insecticide	No	Neonicotinoid	153719-23-4	3.58	4,100	−0.13	NA	6.60E-06	4.70E-10	39	56.2	–
271	Thiaram	Fungicide	No	Carbamate	137-26-8	0.02	18	1.84	8.19	2.00E-02	1.39E-04	15	–	9,629
272	Thiophanate-methyl	Fungicide	No	Benzimidazole	23564-05-8	0.5	18.5	1.4	7.28	9.00E-03	1.67E-04	2	–	220
273	Triadimefon	Fungicide	No	Triazole	43121-43-3	1.59	70	3.18	–	0.02	9.00E-05	–	300	749
274	Triadimenol	Fungicide	No	Triazole	55219-65-3	2.44	72	3.18	NA	0.0005	3.50E-06	64.9	750	273
275	Triasulfuron	Herbicide	No	Sulfonylurea	82097-50-5	4.59	815	−0.59	4.64	0.0021	8.00E-05	38.5	60	12.8
276	Triazophos	Insecticide	No	Organophosphate	24017-47-8	1.38	35	3.55	–	1.33	4.90E-03	9	358	–
277	Trifloxystrobin	Fungicide	No	Strobilurin	141517-21-7	0.15	0.61	4.5	NA	3.40E-03	2.30E-03	1.69	–	2,287
278	Trifloxystrobin acid	Fungicide	Yes	Trifloxystrobin metabolite	252913-85-2	3.57	21,000	–	–	5.50E-03	–	70	–	116
279	Trifluralin	Herbicide	No	Dinitroaniline	1582-09-8	0.13	0.221	5.27	NA	9.5	10.2	170	15,800	8,765
280	Trinexapac-ethyl	Plant growth regulator	No	Cyclohexanecarboxylate derivative	95266-40-3	1.81	10,200	−0.29	4.57	2.16	5.40E-04	14.6	–	280

"–" no available, *NA* no applicable

frequently detected herbicides were ethalfluralin (39% of samples, up to 260 μg kg^{-1}), fluometuron (35% of samples, up to 385 μg kg^{-1}), trifluralin (29% of samples, up to 95 μg kg^{-1}), S-metolachlor (21% of samples, up to 210 μg kg^{-1}), and pendimethalin (4% of samples, up to 29.8 μg kg^{-1}). Quizalofop, fluazifop, and chlorpyrifos were not detected in any of the fields. Overall, the occurrence of herbicides after implementation of the practice was claimed to be lower.

In Switzerland, Chiaia-Hernandez et al. [34] analysed 29 archived soil samples taken over 14 years from agricultural lands and investigated the long-term persistency of 170 CUPs including 80 polar pesticides and 93 TPs. The most prevalent CUPs were simazine (97%, up to 80 μg kg^{-1}), atrazine (86%, up to 249 μg kg^{-1}), tebutam (70%, up to 22 μg kg^{-1}), and carbendazim (72%, up to 61 μg kg^{-1}), and of TPs were atrazine-2-hydroxy (100%, up to 220 μg kg^{-1}), simazine-2-hydroxy +terbuthylazine-desethyl-2-hydroxy (93%, up to 680 μg kg^{-1}), terbuthylazine-desethyl (90%, up to 2 μg kg^{-1}), and atrazine-desisopropyl (86%, up to 9 μg kg^{-1}). Of the pesticides which were applied on lands and detected in archived samples, 45% were detected while applied, and 16% were those applied but not detected. Moreover, 38% of parent pesticides were detected, although they had never been applied on land. It was claimed that even parental pesticides and/or their TPs with lower half-life showed persistence higher than what was expected. In addition, some compounds may occur as impurities in other formulations or as a contamination from adjacent sites. Of the TPs related to applied pesticides, 47% were detected in the soil samples.

A study in the Czech Republic performed by Scherr et al. [49] on soil samples collected from 75 intensively used agricultural fields for residues of 12 chlorotriazine herbicides and their TPs found that the parent compound with the highest maximum concentration and detection frequency (DF) was terbuthylazine with values of 37.6 μg kg^{-1} and 17%, respectively. Atrazine was detected in concentrations less than the limit of quantification (LOQ) and simazine was detected in one sample with a concentration of 8.7 μg kg^{-1}. Major cases of contamination were related to TPs such as 2-hydroxyterbuthylazine (83%, 74.5 μg kg^{-1}), 2-hydroxysimazine (44%, 24.4 μg kg^{-1}), 2-hydroxyatrazine (39%, 123 μg kg^{-1}), and deethylsimazine (12%, 31 μg kg^{-1}). According to the application history of parental pesticides, which stood at 6 months to one decade before sampling for the various compounds, it was stated that the degradation of parent pesticides in soil will produce TPs which are even more persistent than their parent compounds. This result showed the importance of monitoring for TPs besides chemicals used as pesticides in the soil, as they may be more accumulative and persistent than their parent compounds.

In another study, Karasali et al. [50] on 27 soil samples from Greece's central cotton fields, the occurrence and distribution of trifluralin, ethalfluralin, and pendimethalin was investigated. Trifluralin in 44% of the samples (10–210 μg kg^{-1}) and pendimethalin in 7% of the samples (10–48 μg kg^{-1}) were detected. Ethalfluralin was not detected in concentrations higher than the LOQ in any of the samples. These results were obtained while prior to the sampling time, ethalfluralin, trifluralin, and pendimethalin had not been applied to the land for 3 years, 1 year, and 3 months, respectively. This result reveals that some CUPs can be considered as highly persistent in soil and require regular monitoring programs to help improve the pesticide-application system.

Aznar et al. [51] investigated the presence of ten pyrethroid insecticides in 33 samples taken in two sampling periods in plow and cultivation time and two sampling depths of 0–40 and 40–60 cm in a paddy-field area located on the Mediterranean coast (Valencia, Spain). Very high contamination was reported, especially during the rice-cultivation period, which was associated with the waste-water treatment plant used as the source of irrigation of the field. The contamination rate in the rice-production period was higher in comparison with the plow period. The highest contamination was reported for resmethrin and esfenvalerate with 62 and 57 μg kg^{-1} in the rice-production and plow period, respectively. Unexpectedly, it was the subsurface soil layer that was more contaminated by pesticides, rather than the topsoil layer, as resmethrin, rifenthrin, fenpropathrin, ryfluthrin, lambda-cyhalothrin, alpha-cypermethrin, and esfenvalerate were detected in 97–100% and 3–100% of the subsoil samples during the cultivation and plow period, respectively. This is a very firm reason for monitoring soil not only in the plow layer but also in deeper layers of the soil.

Barchanska et al. [52] monitored mesotrione, sulcotrione, and atrazine in 24 agricultural and forest soil samples in Poland. Due the prohibition on atrazine imposed in Poland 7 years prior to the sampling time, it was stated that atrazine did not occur in the soil samples. However, its TPs were detected abundantly in soil samples: deethylatrazine was detected in 46% of soil samples (up to 180 μg kg^{-1}), deisopropylatrazine in 17% (up to 1,640 μg kg^{-1}), and hydroxyatrazine in 42% soil samples, but in concentrations lower than the LOQ. Other compounds which were detected in the soil samples were as follows: sulcotrione in 75% of samples with concentration up to 730 μg kg^{-1} and its TP 2-chloro-4-(methylosulfonyl) benzoic acid (CMBA) in 37% of samples with concentration up to 60 μg kg^{-1}. Neither mesotrione nor its TPs were detected in soil samples. This study was also proof of the importance of monitoring TPs in the soil.

A very broad study on the distribution and occurrence of glyphosate and aminomethylphosphonic acid (AMPA) was performed by Silva et al. [29] on 317 topsoil samples from 11 European Union countries. The countries were chosen from among those with the highest percentage of agricultural area with different crops and the highest amounts of pesticide used per hectare. 21% and 42% of the soil samples contained concentrations higher than LOQ of glyphosate and AMPA in the range of 50–2050 and 50–1920 μg kg^{-1}, respectively. Northern soils were detected with higher DFs and southern soils with higher concentrations for both compounds. On the other hand, in eastern soils a lower frequency of glyphosate and in the southern soils a lower frequency of AMPA were detected. Portugal had the highest DF of glyphosate (53%) and Denmark the highest DF of AMPA (80%). Although no noticeable effect of the crop system was seen, the DF of glyphosate and AMPA was higher in areas under permanent and root crops (30 and 52%) and lower in dry pulses and fodder crops (5 and 29%). Off-site transportation of glyphosate and AMPA is claimed to be a matter of concern as they not only contaminate their surrounding area but can also find their way into all environmental compartments. This is alarming and displays a need for further worldwide programs for monitoring agricultural soils in order to evaluate the occurrence and special distribution of glyphosate and AMPA.

The same soil samples which were subject to analysis for chlorotriazine herbicides by Scherr et al. [49], were analysed for the residue of other active ingredients (53 CUPs and 9 TPs) of different chemical groups by Hvezdova et al. [53] in 75 arable soils in the Czech Republic (CR) several months after the last pesticide application. Almost all the 68 soil samples (99%) were contaminated with at least one of the analysed pesticides or their TPs. Of the 68 analysed pesticides, the residue of 68% was detected in soil samples. Another 32% were absent. Conazole fungicides were the most frequently detected compounds (73% of the soils, up to 65 μg kg^{-1}) in the region. Epoxiconazole (48% of the soils, up to 31 μg kg^{-1}) and tebuconazole (36% of the soils, up to 28 μg kg^{-1}), followed by flusilazole (23% of the soils, up to 19 μg kg^{-1}), prochloraz (21% of the soils, up to 28 μg kg^{-1}), propiconazole (13% of the soils, up to 12 μg kg^{-1}), cyproconazole (8% of the soils, up to 23 μg kg^{-1}), and difenoconazole (7% of the soils, up to 11 μg kg^{-1}) were frequently detected in the soil samples. Chloroacetanilides such as S-metolachlor, metazachlor, or their TPs were other detected chemicals in 25% of the samples (up to 74 μg kg^{-1}). The low-to-moderate water solubility, low pK_a, and high DT_{50} values reported for conazoles were in accordance with the high DF of these compounds. It is claimed that chloroacetanilides and their TPs represented short-term soil contamination due to very short half-lives in the soil and very high mobility. Detected pesticides related to other chemical groups were fenpropidin (20% of soils), diflufenican (17% of soils), urea herbicides (15% of soils), and carbendazim (11% of soils) with maximum concentrations of 62, 51, 92, and 21 μg kg^{-1}, respectively. Chemicals like chlorpyrifos and pendimethalin, which are used in great amounts, were expected to be detected in the samples but were not. The reason was associated with the higher LOD of the analysing method which was reported as 10 μg kg^{-1}.

Glyphosate and AMPA were assessed in a 3-year monitoring study in southern Greece [54]. A total of 170 soil samples from glyphosate-treated as well as non-treated and organic olive farms were analysed for residues. Sampling in conventional sites was done 13–276 days after pesticide application and the mean concentration of glyphosate and AMPA was 14.8 and 54.8 μg kg^{-1} and their DF was 13% and 63%, respectively. In non-treated and organic farms just one sample was contaminated by glyphosate and 11 samples contaminated by AMPA residues. The maximum concentration of AMPA was almost 2 times higher than glyphosate, 650 vs 350 μg kg^{-1}, which indicates that AMPA's degradation was generally slower than its parent compound because it is more likely to be adsorbed to soil.

Silva et al. [30] analysed 74 other pesticides and TPs on the same European agricultural soils evaluated in their previous study [29]. Of all examined soil samples, 83% were contaminated with residues of at least one pesticide or TPs (concentrations >LOQ) and in 53% of the samples with multiple residues of pesticides and/or TPs. In total, 57% of the individual compounds investigated in this study were detected in the soil samples. However, 166 pesticide combinations were presented in the samples. Generally, the most frequently detected CUPs were boscalid (27% up to 410 μg kg^{-1}), epoxiconazole (24% up to 160 μg kg^{-1}), and tebuconazole (12% up to 190 μg kg^{-1}). More frequently detected multi residues were glyphosate + AMPA and glyphosate + AMPA + phthalimide, present in 2% of the samples. Of the pesticide residues detected in the soils, 60% were non-persistent compounds or moderately persistent compounds with DT_{50} less than 30 and 30–100 days, respectively. The soils from root crops and permanent crops had the highest contamination with pesticides, which was in accordance with the reported pesticide use in these crops.

In Northern Portugal, Bragança et al. [55] investigated eight pyrethroids in 18 conventional agricultural sites in two different sampling periods in summer and winter. Deltamethrin was the only pyrethroid detected in soil samples (8% of soil samples) with concentration up to 101.7 μg kg^{-1}. It occurred only in the summer sampling.

Kosubova et al. [33] investigated 53 CUPs in 136 soil samples from 34 sites in Czech Republic. It was part of a 4-year monitoring program for the occurrence of 60 pesticides and four TPs across space and time. Of the analysed compounds, 19 were not detected in any of the samples mainly due to the ban or restrictions on their use prior to the sampling time or their short half-lives. These compounds included some important compounds such as atrazine and its TP desethylatrazine, acetochlor, metalaxyl-M, promethryn, and 2,4-D. On the other hand, more than 50% of the samples contained a mixture of 2–7 chemicals in 116 different multiple-residue combinations. In all the sampling years, atrazine TPs were present and detected in 44–71% of the soil samples which, it is claimed, was due to the previous applications on the sampling area. Current application of terbuthylazine products also caused contamination of atrazine, because atrazine can occur as an impurity in terbuthylazine formulations. This result again emphasizes that TPs may be more persistent than their parent compounds. Pendimethalin (up to 310 μg kg^{-1}), diflufenican (up to 160 μg kg^{-1}), tebuconazole (up to 140 μg kg^{-1}), chlorotoluron (up to 90 μg kg^{-1}), and linuron (up to 80 μg kg^{-1}) were the compounds with the highest residue concentrations in the soil samples. High DFs in each sampling year were reported for epoxiconazole with a DF range of 57–62% (up to 32 μg kg^{-1}) and tebuconazole with a DF range of 35–47% (up to 140 μg kg^{-1}) and not in accordance with their rate of application to the soil. The occurrence of the banned pesticide carbendazim was attributed to its long half-life in soil (DT_{90} of up to 257 days in soil) and degradation of thiophanate-methyl.

In the upper part of the river Elbe, Germany, Karlsson et al. [56] investigated 20 soil samples from the floodplain area for pesticides of different chemical groups. The only detected CUPs were simazine (100%, up to 0.061 μg kg^{-1}) and ethofumesate (30%, up to 23.25 μg kg^{-1}), along with two TPs 2-hydroxy-atrazine (100%, up to 6.61 μg kg^{-1}) and 2-hydroxyterbuthylazine (100%, up to 0.75 μg kg^{-1}). The two parent compounds were also present in the water-monitoring database. Atrazine, known as a relatively persistent compound, was not found in the soil, while its main TPs were present. This was related to the periodical floods, which led to suspending or dissolving contaminations from the stream into the floodplain soil.

Ukalska-Jaruga et al. [57] examined 216 arable soil samples from Poland for the presence of organochlorine and non-chlorinated pesticides. Higher concentrations and DFs were reported for carbaryl and atrazine with values equal to 28.07 and 15.85 μg kg^{-1} and 20 and 80%, respectively. Maneb was absent in all the soil samples. The total residue of non-chlorinated pesticides was reported to be up to 43.92 μg kg^{-1}.

In Belgium, soil samples from 18 fruit orchards (apple and cherry) were monitored for 70 active ingredients, including 35 insecticides, 22 fungicides, and 13 herbicides, of which 66% were detected in the soil samples [58]. Boscalid, carbendazim, and difenoconazole were detected in all soil samples (DF = 100%) with concentrations up to 10,990, 3,279, and 1,480 μg kg^{-1}, respectively. Other compounds frequently detected in the soil samples were tebuconazole (99%, up to 1,472 μg kg^{-1}), imidacloprid (97%, up to 112 μg kg^{-1}), linuron (97%, up to 1,280 μg kg^{-1}), diuron (89%, up to 225 μg kg^{-1}), and pyraclostrobin (86%, up to 203 μg kg^{-1}).

3.2 Monitoring and Survey Studies in Asia

Liu et al. [59] analysed the residues of 29 pesticides including CUPs in 46 soil samples from persimmon and jujube farms in China. Of 10 detected CUPs, the most frequently detected were fenpropathrin (50%, up to 400 μg kg^{-1}) deltamethrin (47%, up to 46.9 μg kg^{-1}), cyhalothrin (47%, 16 μg kg^{-1}), cypermethrin (45%, 44.7 μg kg^{-1}), bifenthrin (41%, 18.3 μg kg^{-1}), triadimefon (28%, 94.5 μg kg^{-1}), and chlorpyrifos (8%, 25.5 μg kg^{-1}). In this study, corresponding fruit samples were also analysed for the residues. Comparison showed that the DF of detected CUPs in soil was higher than in fruit samples. Multiple residues were frequently observed in soil samples, whereas up to 14 combinations were detected in some soils due to the higher persistence of compounds in the soil and secondary contamination from neighbouring areas.

In an article by Rafique et al. [60] high soil contamination with CUPs was reported. This study was carried out on 90 samples collected from cotton/wheat farmlands in Okara district, Pakistan. The main contaminations were imidacloprid and chlorpyrifos with DFs equal to 74 and 66%, and maximum concentrations equal to 1950 and 1993 μg kg^{-1}, respectively. MCPA (methyl ester) (29%, up to 1,531 μg kg^{-1}), deltamethrin (34%, up to 1,184 μg kg^{-1}), bifenthrin (20%, up to 884 μg kg^{-1}), and α-cypermethrin (49%, up to 774 μg kg^{-1}) were other CUPs with higher residue concentration.

In the same region studied by Liu et al. [59], 38 nut-planted soils of China were analysed for pesticides of different chemical groups by Han et al. [61]. The abundantly detected pesticides were pyrethroids, such as triadimefon (71%, up to 193.7 μg kg^{-1}), bifenthrin (63%, up to 156.3 μg kg^{-1}), cypermethrin (60%, up to 70.4 μg kg^{-1}), buprofezin (52%, up to 807.4 μg kg^{-1}), fenvalerate (47%, up to 884 μg kg^{-1}), and fenpropathrin (39%, up to 143.8 μg kg^{-1}). Chlorpyrifos was the only detected organophosphorus pesticide in 5% of the samples up to 77.2 μg kg^{-1}. Chlorpyrifos and fenvalerate were two pesticides widely used in the region according to local farmers. This was in accordance with their occurrence in the soil samples. Multiple-residue pesticides were detected in 73.7% of the samples.

Kailani et al. [62] reported that in monitoring 448 CUPs in 100 soil samples from southern Jordan, metalaxyl (37%, up to 2,660 μg kg^{-1}), difenoconazole (24%, up to 1700 μg kg^{-1}), imidacloprid (22%, up to 2,380 μg kg^{-1}), and azoxystrobin (17%, up to 460 μg kg^{-1}) were the most frequently detected CUPs. The compounds with the highest concentration were oxyfluorfen (2%, up to 6,490 μg kg^{-1}), pyridaben (12%, up to 5,820 μg kg^{-1}), and chlorfenapyr (12%, up to 4,990 μg kg^{-1}).

Pan et al. [63] studied 530 soil samples from orchard and vegetable farms of a major agricultural area in North China for residue of 47 CUPs. The most frequently detected CUPs were tebuconazole with DFs of about 60%, then difenoconazole, chlorpyrifos, and thiamethoxam with DFs of approximately 25 to 30%. In concentrations above 100 μg kg^{-1}, atrazine was the pesticide present in the highest number of soils (3.4%). Orchard fields were revealed to have the most contaminated soil (60% of the most contaminated locations). This proved higher pesticide use on orchards in comparison with other crops.

In central China, Pan et al. [64] collected 60 soil samples from two soil layers. Chlorpyrifos with a maximum concentration up to 5.58 μg kg^{-1} was the only CUP occurring in both layers. The high evaporation and water solubility of analysed CUPs were considered as the main reason for the obtained result.

Bhandari et al. [65] presented the concentration and distribution of residues of 23 pesticides analysed in 147 soil samples from IPM and conventional vegetable-growing lands in Gaidahawa rural municipality Nepal. Seventy-five per cent of conventional farms and 15% of IPM farms were found to be contaminated by pesticides. The lower contamination of IPM fields with pesticides was attributed to the efficiency of the IPM method, yet it was also stated that due to lower organic carbon content in IPM fields, chemicals were more likely to leach into the groundwater. It was stated that 15 pesticides and/or TPs in 39 combinations were present in the 60% of the soil samples, of which 60% were non-persistent or moderately persistent.

Pico et al. [66] did a study on the occurrence of 59 CUPs in the soil of lagoon wetland in Saudi Arabia. The region was said to be affected by wastewater discharge from agricultural activities. The residue of five compounds was detected in ten soil samples as follows: chlorpyrifos (100%, up to 0.84 μg kg^{-1}), chlorfenvinphos (40%, 0.84 μg kg^{-1}), fenitrothion (10%, up to 56.1 μg kg^{-1}), carbendazim (10%, 0.04 μg kg^{-1}), and imidacloprid (10%, 0.28 μg kg^{-1}).

In the soil of 11 randomly collected soil samples from tea-plantation sites in the wet and dry season in Indonesia, Ariyani et al. [67] analysed the residues of five pyrethroids (lambda-cyhalothrin, permethrin, cypermethrin, fenvalerate, and deltamethrin) using a validated proposed method. The only detected compounds were permethrin and deltamethrin with DFs equal to 68 and 50% in all samples and a maximum concentration of 360 and 120 μg kg^{-1}, respectively. Mostly, the concentration of permethrin was higher than deltamethrin in the soil samples and the average concentrations of both were higher in the wet season. In the dry season no residue of deltamethrin was found, a fact which was associated with its shorter half-life in comparison with other pyrethroids.

3.3 Monitoring and Survey Studies in America

Bortolozo et al. [68] monitored five CUPs in 108 soil samples taken at three depths from Ponta Grossa peatland. The major contaminants were atrazine (17%, up to 1 μg kg^{-1}), chlorpyrifos (14%, up to 0.6 μg kg^{-1}), and lambda-cyhalothrin (10%, up to 0.5 μg kg^{-1}). In a deeper layer (over 30 cm) no residue of analysed CUPs was detected. The number of detections in the soil samples was 1.6 times more than water well samples. This was due to the high tendency of the analysed pesticides to bond to the soil's organic carbon.

In southeast of the Entre Rios Province, Argentina, Primost et al. [69] found that 100% of the soil samples collected from 17 agricultural farms had residues of both glyphosate and AMPA in concentrations up to 8,105 and 38,939 μg kg^{-1}, respectively. In this study, lower DFs were reported for surface-water samples in comparison with soil samples and no detection was reported for groundwater samples.

3.4 Monitoring and Survey Studies in Africa

The only study determining pesticide residues in African soils during the last 5 years was carried out in Sokoto state, Nigeria [70]. In the 17 number of soil samples, 13 organophosphate and organochlorin pesticides were analysed. It found that chlorpyrifos was the most abundant CUP, and it was detected in high concentrations in soil samples with a DF of 88% and maximum concentration of 2,870 μg kg^{-1}. Dimethoate (59%, up to 1870 μg kg^{-1}), dichlorvos (53%, up to 1,180 μg kg^{-1}), mevinphos (53%, up to 1,000 μg kg^{-1}), and methyl-parathion (53%, up to 1910 μg kg^{-1}) were other CUPs with high DFs and concentrations.

4 Future Perspectives

According to the findings of this review, the level of soil contamination with CUPs in many regions is worrying. In some of them the situation is even worse, and countries still show a significant disparity in the inspecting strategies applied. Also, no significant improvement in the number of studies dedicated to the monitoring of CUPs in the soil has been observed after some time has passed. For instance, in Africa in which great amounts of CUPs were present, a lower number of monitoring studies have been performed during the last few years. Moreover, due to the unknown complex behaviour of CUPs in different compartments and their ability to undergo long-range transportation, a wise response to CUP contamination would be regular monitoring of the soil not only in specific regions, but also at a global scale. The results also showed that under specific conditions, CUPs' properties in the soil differ of some expectations, i.e. a half-life longer than expected was reported for some compounds, which makes these chemicals more persistent and accumulative in the soil. Furthermore, the results presented that the degradation of CUPs such as atrazine led to TPs, which were even more persistent than their parental compounds. The results showed that monitoring of TPs in the soil is as important as tracking their parent compounds and must be included in monitoring programs. Clearly, there is insufficient research dedicated to monitoring CUPs in soil and there is an enormous need worldwide. As a result, future research is recommended to meet this need on the occurrence and fate of CUPs in the soil.

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An Overview of Recent Research on the Role of Dissolved Organic Matter on the Environmental Fate of Pesticides in Soils

Aránzazu Peña, José Antonio Rodríguez-Liébana, and Laura Delgado-Moreno

Contents

Abstract Pesticides reach the soil after direct application to the soil surface or after deposition from the treated crops. The environmental behaviour of pesticides in soil has been usually related to organic carbon and clay contents of soils. However, interest is growing in knowing how pesticide fate may be modified by dissolved organic matter (DOM) coming from a variety of sources, such as irrigation with solutions rich in DOM, leachates from organic amendments or plant litter. In this

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chapter the current extent of DOM impact on pesticide adsorption/desorption, transport or dissipation in soil is reviewed first and the findings contrasted with DOM origin or properties. The consequences of DOM on pesticide crop uptake are also discussed. Main gaps in knowledge stem from the complex composition of DOM originating from a wide variety of sources and its specific interactions with pesticides and soils that deploy an ample range of properties. A final summary of findings and implications for future research is also included.

Keywords Agricultural soils, Dissolved organic matter, Environmental behaviour, Organic amendments, Pesticide

1 Introduction

Pesticides, used for pest and weed control, reach the soil because they are either applied directly on the soil surface or else deposited on the soil after spraying the target crops [1, 2]. In addition, they may indirectly reach the soil by transportation from other compartments such as atmospheric or runoff deposition [3, 4], or with the irrigation water [5]. Processes affecting the dynamics of pesticides in soils have been usually associated with the soil content in organic carbon (OC) and minerals (clays, oxides and hydroxides) [6, 7]. However, they may be also influenced by the presence of dissolved organic matter (DOM), as reviewed in depth in the following sections.

In recent years, several reviews have been published dealing with the effect of organic matter (OM) on pesticide fate in soil. However, while most of them describe how exogenous OM (mostly in the form of straw, manure, compost or biochar) affect pesticide behaviour, they only sporadically delve into the role of DOM [8–10] or else review the effect of a single type of DOM, like DOM from crop straw [11], wastewater [12] or humic substances [13].

Therefore, this chapter intends to fill these gaps and includes the most recent scientific articles, from 2015 onwards, dealing with this subject. For this purpose, this chapter includes two main sections. The first section presents the main DOM properties related to pesticide behaviour in soils. Special attention is deserved to the different sources of DOM and their role in the soil DOM composition and concentration. The second section makes a compilation of the more recent articles dealing with the effect of native or exogenous DOM on the main processes affecting the fate of pesticides in soils (i.e., adsorption/desorption, leaching, dissipation and crop uptake), which ultimately determine the presence of these organic pollutants in other environmental compartments.

2 Sources, Composition and Concentration of DOM in Agricultural Soils

DOM is relatively low abundant (<0.25%) with regard to total soil OM [14] but, due to its high mobility and reactivity, it plays an important role in biogeochemical processes, particle stability and transport of organic and inorganic contaminants in soil with important implications in water and soil pollution [15–17]. The chemical and structural characteristics of DOM, as well as its concentration, are the most important parameters affecting the behaviour of organic contaminants such as pesticides in soils [18, 19]. Furthermore, the surface charges of DOM may play a fundamental role in the binding of pesticides with ionic character.

In this section, we delve into the sources, concentration and composition of DOM in agricultural soils to get some insights that contribute to understand the effect of DOM on the dynamics and interactions of pesticides in soils.

DOM is defined as the OM remaining in solution through a 0.45 μm filtration [20]. It is frequently quantified by its carbon content and referred to as dissolved organic carbon (DOC). DOM can be characterised by an ample array of analytical methods, which are informative on their own and complement each other [11, 21]. Therefore, it is desirable to integrate multivariate information to understand better DOM nature.

DOM is composed by a broad array of aromatic and aliphatic molecules containing oxygen, nitrogen and sulphur functional groups (e.g. carboxyl, phenol, enol, alcohol, carbonyl, amine and thiol) [22, 23]. In general, the composition of soil DOM reflects that of total soil OM, since both the soluble and solid phases tend to be in equilibrium [24]. More particularly, in agricultural soils DOM mainly consists in low molecular weight (LMW) compounds such as carboxylic acids, amino acids, carbohydrates and fulvic acid (FA), which is an abundant fraction of DOM [25, 26]. Intermolecular interactions between DOM and other molecules with different functional groups change the chemical and physical properties of DOM and thus, determine its size, shape and polarity, which ultimately influence the binding with pollutants [23, 27]. Among other physicochemical parameters, temperature, pH, ionic strength and type of ions in solution affect molecular interactions of DOM and dictate its dynamics in natural environments [25, 28]. In addition, higher concentrations have been directly related to DOM aggregation, leading to slower diffusion, larger particle size and greater colloidal stability [23, 29].

The source of DOM is the primary factor that determines its concentration and composition. In agricultural soils, DOM comes mainly from crop litter, root exudation and the application of organic amendments such as manure, compost, biosolids and biochars [26, 30–32]. Long-term irrigation with wastewater effluents is also considered as an important source of DOM [12], as well as microbial metabolism and the turnover of microbial biomass [26, 33, 34] (Fig. 1). Thus, Steenwerth and Belina [35] analysed the effect of crop cover on DOM and microbial biomass carbon in a vineyard soil during a year. These authors found that the increase in DOC in summertime could be partially explained by the decrease of microbial biomass

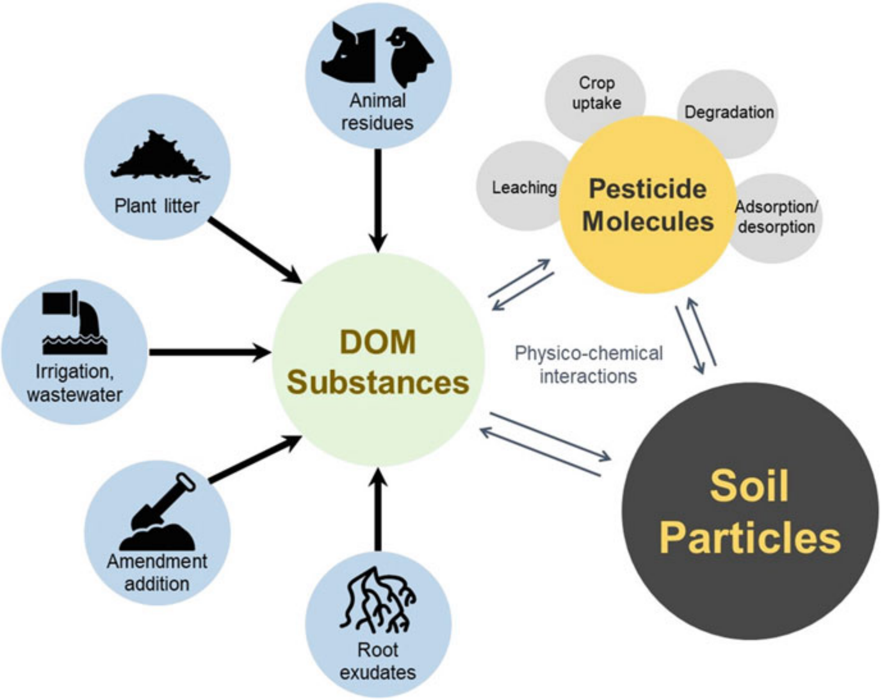

Fig. 1 Main sources of dissolved organic matter (DOM) in agricultural soils and pesticide processes, reviewed in this chapter, affected by soil–DOM–pesticide interactions

carbon by turnover. Linked to this, the fluorescence index (the ratio of emission intensity at 450 nm over 500 nm at 370 nm excitation) has been used to distinguish microbially from terrestrially derived DOM sources [22]. Carpio et al. [36] concluded that amendment of an agricultural soil with spent mushroom substrate or green compost resulted in initial higher values of microbial community's total biomass that decreased over time.

The concentration of DOC in the soil solution is controlled by adsorption/ desorption, precipitation/dissolution, decomposition, diffusion, complexation/ decomplexation, and protonation/deprotonation processes [37]. Besides the source of DOM, environmental factors such as climate, hydrology and soil properties govern the balance (production and removal) of DOM in soils and its presence in soil leachates and pore water [30]. Liu et al. [38] found that precipitation is the main factor controlling DOC concentration through leaching, dilution and indirectly through affecting DOM biological decomposition. Regarding soil properties, pH and ionic strength determine the solubility of DOM, whereas the content of Fe, Al, clay and OC and the cation exchange capacity influence the adsorption/desorption of DOM into the soil matrix and, therefore, the presence of DOM in the soil solution and leachates [39–42]. Finally, hydrology controls the drainage and lateral export.

Since the content of DOM depends on different factors as described above, soil-derived DOC concentration in either pore water or soil leachates varies significantly among different ecosystems [43], being its content lower in arable soils than in forest or grassland soils mainly due to the type of vegetation [25]. Zsolnay [24] indicated that DOC concentration in agricultural soils varies from 0 to 70 mg L^{-1}. However, the application of organic amendments, a common agricultural practice, contributes to an immediate and significant increase in soil DOC content [43–47]. This is generally attributed to the presence of soluble materials in the amendments, which depends on the amendment nature [48], and can vary from 2.4 g C kg^{-1} for sewage sludge to 133 g C kg^{-1} for spent mushroom substrate [26]. Despite that several studies have demonstrated that these soluble materials are easily decomposed and soil DOM is rapidly returned to background level [36, 45, 49–51], the continuous application of amendments has resulted in an increase of the DOM content in agricultural soils by 11–1,013 kg ha^{-1} [52, 53]. In addition, organic amendments may change soil properties such as pH, which could favour the dissolution or desorption of native soil DOM [54].

The composition of soil DOM is also influenced by the type of organic amendment applied to soil. Ohno and Crannel [55] found higher MW in DOM from animal manure (2000–2,800) than from plant residues (710–850), although the former was less reactive. Larger MW and extended aromatic polycondensation were also reported for composted amendments with regard to the raw materials [56]. Composts from four different sources (manure, sewage sludge, kitchen and green wastes) revealed 23% ubiquitous DOM but also relevant source-specific signatures [43]. Plaza et al. [57] observed that the FA fraction of DOM extracted at different times during the co-composting of a mixture of olive-oil mill sludge and tree cutting increased in N, O, COOH and phenolic OH contents, C/H and O/C ratios and aromaticity and decreased in C, H, and S contents, C/N ratio and aliphaticity. During the composting process, as the organic substrate is transformed into humic-like materials, compounds of increasing molecular complexity and structural homogeneity are produced [56, 58]. The aromatic nature of humic substances makes them especially effective binders of some organic pollutants like pesticides. This binding, which has been shown to be compound-specific, would explain the enhanced solubilisation in aqueous ecosystems [13]. For instance, humic acids (HA) exhibited very strong adsorption affinity (>68%) to polar and ionisable pesticides, like the phenoxyacetic acids 2,4-D and MCPA, because of specific interactions of the pesticides with active HA functional groups [59]. The interactions were much weaker (10–35%) for the nonionic carbamate pesticides carbaryl and carbofuran.

Similar to DOC content, the single application of organic amendments modifies the composition of soil DOM. However, this modification is unlikely to be permanent since added DOM is mineralised over time through extended microbial oxidation, and only the most recalcitrant components such as aromatic and S-containing structures are incorporated to soil OM [60]. In contrast, the continuous application of organic amendments may significantly change the soil OM, affecting the soil-derived DOM. Thus, the repetitive application of municipal waste compost to a soil during 9 years increased the N, S and aliphatic contents and decreased the C/N ratio and O and acidic functional group contents of soil OM [61]. A reduction in acidic functional groups and a slight increase of proton-binding affinities of carboxylic and phenolic type groups were also observed in FA isolated from soils amended with either composted or thermally dried sewage sludge for 3 years [62]. These changes in FA composition were more evident in soils amended with composted than with dried sewage sludge. Other studies have also reported changes in soil DOM composition after long-time organic amendment applications [63, 64]. Musadji et al. [65] showed that long-term addition of urban and green composts increased DOM concentration but did not result in a major change in DOM composition, the quantity depending on the season and the quality on the specific amendment. A wide geographical area in China was selected to study the effect of the application of straw return and inorganic fertilisation on extractable humic substances [66]. Geographical location rather than fertilisation practice dominated the spatial variation of the chemical composition of humic substances.

Biochars are gaining increased attention as amendments in soils for, among other things, their ability to sequester carbon, improve water retention and nutrient levels and activate microbial biomass [9, 32, 67–69]. A further characteristic of biochars, with agronomic and environmental implications, is their high affinity for organic contaminants [70]. Moreover, biochars seem to be a significant source of mobile OM, because their use as soil amendments can increase the amount of DOM in the soil pore water [71–73], hence potentially impacting pesticide behaviour especially in soils subjected to periodical flooding irrigation. FTICR-MS analysis showed that the MW and aromatic components of the DOM in a biochar from straw were higher than those from natural straw [74]. Other studies reported preferential occurrence of protein-like components in the binding of some organic contaminants [73].

When the exogenous DOM is added with the irrigation water the effects on soil DOM are inconclusive. It has been recently suggested that processes occurring in the soil ecosystems (e.g. root exudation or microbial respiration) influence the properties of soil DOM to a larger extent than the nature of the DOM in the irrigation water [75]. In line with this, other works found that irrigation of soils with treated wastewater for 7 years [76] or with untreated wastewater for 35 and 85 years [77] had insignificant effects on the amount in soil of both total and dissolved OC. On the other hand, the opposite effect, that is, increased soil total OM or DOM by long-term irrigation with wastewater has been also reported [78–81]. It is deduced from these works that, irrespective of the nature and content of DOM, the ability of soil to assimilate the OM added must be taken into account. Therefore, further research is required to understand accurately the complexity of the mechanisms involved.

Apart from the addition of exogenous OM, DOM concentration and composition in agricultural soils are also influenced by other agricultural management practices such as liming, tillage and mineral fertilisation [26, 66, 82]. Changes in DOC caused by these agricultural practices are generally of short duration while long effects are mainly related to the return of organic carbon to soils from litter and organic amendments [25].

3 Pesticide Fate in Soil under DOM Influence

3.1 Adsorption/Desorption

In soils, adsorption is defined as the passage of a sorbate from the soil solution to the soil matrix without causing changes in its composition. Desorption, which represents the inverse process, is negatively related with the adsorption energy, which determines the reversibility of adsorption. Because of this, adsorption/desorption phenomena are generally deemed as the most important modes of interaction between soil and organic pollutants, and control the concentration of the latter in the soil solution. Since adsorption/desorption affects the rest of the processes involved in the fate of contaminants in soils, understanding the mechanisms involved is of utmost importance to monitor and predict their potential to reach surface and groundwater resources [6].

Two or more mechanisms may occur simultaneously depending on the pesticide-soil system [83]. In addition, the presence of DOM in the soil solution may interfere in this process. In this sense, DOM has been extensively reported to alter differently the retention behaviour of pesticides depending on not only the physicochemical properties of the chemicals, but also the source, properties, composition and concentration of DOM, as indicated in Sect. 2 of this chapter. However, although extensively studied, the role of DOM in the fate of organic pollutants such as pesticides is still not sufficiently understood since it depends on the specific DOM-pesticide-soil system. Due to this multiplicity, it seems tough to establish consistent role models to predict the effects of DOM in the sorption behaviour of pesticides.

As aforementioned, some parameters related with DOM such as the concentration, MW, polarity or sources, which in turn determine its composition, are the major factors affecting the retention of pesticides by soils. Table 1 gathers the last reports concerning the effects produced by DOM in the adsorption/desorption of pesticides in soils. For instance, Tian et al. [84] assessed the effects of DOM extracted from rice straw in the adsorption and desorption of atrazine in soil. Their results showed decreased adsorption and enhanced desorption of the herbicide with the increasing concentration of DOM in the solution. However, the mechanisms involved in the process were not investigated. In a similar approach, DOM extracted from three different sources (one of the soils in the study, DOM_P; a fresh-prepared organic compost, DOM_C; and rice straw, DOM_R) inhibited adsorption and increased desorption of the acidic herbicide MCPA in three types of ferralsols [85]. This behaviour was positively and negatively correlated with the hydrophobic and hydrophilic DOM fractions, respectively. Therefore, DOM_C and DOM_R produced the strongest and weakest effect, respectively, in accordance with their hydrophobic/hydrophilic balance. After SEM and FTIR analysis, the authors concluded that both pore blocking by DOM sorption on soil surface and enhanced solubility caused by specific MCPA–DOM interactions in the liquid phase were the mechanisms responsible for reduced adsorption. In addition, electrostatic repulsion between DOM, which becomes negatively charged after sorption to soil, and the herbicide was

Table 1 A summary of the effect of DOM from different sources on the adsorption-desorption of pesticides in soil

	Pesticide properties[c]			Soil properties					
Pesticide	Ws ($mg\ L^{-1}$)	Log Kow	pK_a	Sand:clay (%)/ OC, OM (%)/ pH	DOM source	DOC content ($mg\ L^{-1}$)	Experimental design	Main results	Ref.
Atrazine	35	2.7	1.7	31:31/1.3/7.6	Extracted from rice straw	60 and 180	Adsorption-desorption isotherms	Decreased adsorption and enhanced desorption of atrazine at increasing DOC concentration in the liquid phase	[84]
MCPA	29,390	−0.81	3.73	20:50/0.68/5.8 30:37/1.6/7.5 82:16/1.0/5.8	Extracted from soil, compost and rice straw	20	Adsorption-desorption isotherms	Decreased adsorption and increased desorption caused by soil pore blocking and enhanced solubility of MCPA. Strongest and weakest effects for compost-DOM and rice straw-DOM respectively. Some DOM fractions played relevant roles	[85] [86]
Fenobucarb Endosulfan *p-p'*-DDT	420 0.32 0.025	2.78 4.75 6.91	– – –	7:29/1.8/5.1	Extracted from compost Surfactant (SDS) Sodium oxalate	8–92 0–6.4 CMC[a] 0–0.15 M	Simultaneous effect of DOC, surfactant (SDS) and sodium oxalate. Single-point	Combined effect of DOM with surfactant and sodium oxalate represented by quadratic	[87]

							desorption assays. Soil previously spiked with the insecticides and desorption with different solutions	regression equations. Higher desorption of the pesticides, especially for the less hydrophobic compound, when increasing DOC concentration	
Imazalil	184	2.56	6.49	17:33/8.7/5.6 12:13/2.1/7.4 27:8/3.0/5.4	Gallic acid	25–400	Single-point adsorption tests. Differences in the adsorption are evaluated in native and biochar-amended soil (0.5%)	Adsorption is higher in amended soil. In native soil, sharp adsorption increase at low concentrations of gallic acid, and gradual adsorption increase at higher acid concentrations. This effect disappears in the amended soil, for which adsorption of imazalil levelled off at 100 mg L^{-1} gallic acid	[88]
Atrazine	35	2.7	1.7	n.a. (black soil)	Extracted from the soil assayed	75.65, in soil extract. Three-fold dilution for the adsorption experiments	Adsorption kinetics and isotherms	Enhanced adsorption of atrazine related with humic-like substances in DOM, which represent the major fraction	[89]

(continued)

Table 1 (continued)

Pesticide	Pesticide properties[c]			Soil properties	DOM source	DOC content (mg L^{-1})	Experimental design	Main results	Ref.
	Ws (mg L^{-1})	Log Kow	pK_a	Sand:clay (%)/ OC, OM (%)/ pH					
Atrazine	35	2.7	1.7	n.a./~2/~6 for both non-rhizosphere and rhizosphere soils	Rhizosphere soil *P. americanum* (root exudates)	n.a.	Adsorption kinetics and isotherms	Enhanced adsorption related with alterations in the concentration and nature of DOM due to root exudates in the rhizosphere soil	[90]
Tebuconazole Glyphosate	36 10,500	3.7 −3.2	5.0 2.34	38–100:0–14/ 0.05–0.89/7.2–8.5	Liquid pig manure	26.5–265	Adsorption isotherms in different soil profiles	Variable effects for tebuconazole depending on DOM binding to soil surface (co-sorption phenomena). Strong decrease of glyphosate adsorption due to the presence of DOM from liquid pig manure in the solution	[91]
Dichlorvos Chlorpyrifos	18,000 1.05	1.9 4.7	– –	Sandy soil/0.7/ 8.5	Compost from mixed wastes, dried goat manure, and commercial HA	354 (compost) 620 (manure) 100–1,000 (HA)	Soil amended with both organic residues (2.5 and 5% rates). Adsorption isotherms	Different DOM sources produced a non-significant adsorption increase for dichlorvos and substantial adsorption reduction for	[92]

								chlorpyrifos. Interactions with the pesticides are determined by the aromatic and humic fraction of DOM	
Oxyfluorfen	0.12	4.86	–	71:20/0.6/8.1 (S1, native) 71:20/2.0/7.6 (S1, amended) 6:52/1.0/8.1 (S2, native) 6:52/2.2/8.1 (S2, amended)	Olive-oil mill waste	50–230^b	Adsorption-desorption isotherms. Soils amended with olive-oil mill waste (5% rate)	Regarding unamended soils, lower adsorption into the one that released a greater DOC amount. Adsorption increased at variable extent in amended soils depending on the increase of soil OC and on the amounts of DOM released from soils. Desorption was not affected	[93]
Diuron	35.6	2.87	–	30:35/1.4/8.1 67:9/0.5/5.6	Three composts	The composts contained 38.3–45.4% OC and 32.8–69.7 g kg^{-1} DOC	Soils amended with the composts at a rate of 12.5 mg OC g^{-1} soil. Single-point adsorption tests	Adsorption increased in amended soils. Both the amount and the chemical nature of the DOM released from the amendments played a crucial role	[94]

(continued)

Table 1 (continued)

Pesticide	Pesticide properties[c]			Soil properties	DOM source	DOC content ($mg\ L^{-1}$)	Experimental design	Main results	Ref.
	Ws ($mg\ L^{-1}$)	Log Kow	pK_a	Sand:clay (%)/OC, OM (%)/pH					
Tricyclazole	596	1.4	–	20:36/2.4/8.2	Alperujo compost and biochar	The compost contained 55.12% OM and the biochar 4.5 $mg\ L^{-1}$ DOC	Soil amended with compost or biochar (2% rate), or with compost/biochar mixture (1% each). Sorption-desorption isotherms	Adsorption of tricyclazole increased with the amendments, but the lowest adsorption obtained for the soil amended with the compost was explained by the higher DOM amount released to the soil solution	[70]
Bentazone Pyraclostrobin Aminocyclopyrachlor	7,112 1.99 3,130	−0.46 3.99 −2.48	3.51 – 4.6	22:23/2.5/6.0	Different biochars from wood chips pellets, macadamia nut shells and hardwood	14–352	Soil amended with biochars (10% dose). Sorption-desorption isotherms	Variable effects depending on DOC concentration and properties. Biochars releasing higher amounts of DOC and/or DOM with higher humification index disfavoured pesticide adsorption	[95]

Azimsulfuron Penoxsulam	1,050 408	−1.4 −0.60	3.6 5.1	n.a.:28/1.7/5.4 n.a.:28/2.1/6.7	Two biochars from composted alperujo	545–2,820	Soils amended with biochars (5% rate). Sorption-desorption isotherms	Variable effects depending on soil, biochar and pesticide properties. Azimsulfuron adsorption correlated with the amount and composition of DOC. The water-extractable substances of biochar modified azimsulfuron adsorption but did not interfere with penoxsulam behaviour	[67]
Simazine Diuron	5.0 35.6	2.3 2.87	1.62 –	11–90:2–48/ 0.02–1.6/8.1–9.3 (data from control soils)	Olive-oil mill WW	26,000–35,000	Soils traditionally polluted with WW. Single-point adsorption experiments	Higher adsorption in polluted soils is found especially for diuron that yielded specific interactions with DOM from WW bound to soil	[96]

(continued)

Table 1 (continued)

Pesticide	Pesticide properties[c]			Soil properties	DOM source	DOC content (mg L^{-1})	Experimental design	Main results	Ref.
	Ws (mg L^{-1})	Log Kow	pK_a	Sand:clay (%)/ OC, OM (%)/ pH					
Diuron	35.6	2.87	–	22:37/n.a./n.a.	Olive- oil mill WW	26,000	Field experiment consisting of four seasonal applications of WW. Single-point adsorption experiments	WW application induced enhanced K_d, probably by increasing soil OC. However, a clear relationship was not found, and changes in soil OM nature due to WW application were also postulated	[97]
Dimethenamid Fenarimol	1,200 13.7	2.2 3.69	– –	31:11/1.2/8.1 10:51/0.62/7.9 26:33/0.91/8.1	Urban WW Extracted from sewage sludge	25 (WW) 30–300 (sludge)	Soil irrigation with WW and sewage sludge extracts. Adsorption-desorption isotherms	No effect of WW on pesticide adsorption. Enhanced adsorption of fenarimol with increasing concentration of DOC from sludge in solution. WW and DOC at 300 mg L^{-1} increased desorption of dimethenamid	[98]

Thiacloprid	184	1.26	–	31:11/1.2/8.1	Urban WW Extracted from sewage sludge	25 (WW) 3–300 (sludge)	Soil irrigation with WW and sewage sludge extracts. Adsorption-desorption isotherms	No effect of WW on thiacloprid adsorption. Adsorption tends to decrease at higher DOC concentrations from sludge in the soil solution	[99]

Ws water solubility, *Log Kow* octanol/water partition coefficient, *OC/OM* content in organic carbon/matter, *DOC/DOM* dissolved organic carbon/matter, *n.a.* not available, *WW* wastewater

[a] CMC, critical micellar concentration

[b] DOC in mg kg^{-1}, K_d soil-water partition coefficient

[c] Pesticide properties from PPDB (https://sitem.herts.ac.uk/aeru/ppdb/en/atoz.htm)

postulated. Very recently, the same authors concluded that both the hydrophobic neutral DOM fraction and acid insoluble DOM induced the highest soil pore blockage, because both fractions contain humic-like substances with high aromaticity and MW. On the contrary, the hydrophobic acid fraction led to the highest solution enhancement of MCPA, due to its content in aromatic acid and polar groups [86]. Similarly, the simultaneous addition of compost-derived DOM, the anionic surfactant sodium dodecyl sulphate and sodium oxalate resulted in an increased desorption of the insecticides fenobucarb, endosulfan and *p,p'*-DDT from the surface layer of a paddy soil [87]. The main finding of this study is that the higher the concentration in the solution of DOM, surfactant or sodium oxalate, the higher the desorption of the insecticides from the soil. Worthy to mention is that the increase in the concentration of DOM seems to impact more the behaviour of fenobucarb, of intermediate polarity, than that of the other two hydrophobic insecticides.

In contrast with the previous studies, promoted pesticide adsorption in the presence of DOM has been also reported. For instance, He et al. [88] found increased adsorption of the weakly acidic fungicide imazalil in soil with increasing concentration of gallic acid used as DOM. Imazalil adsorption enhanced from 32.9 to over 50 mg kg^{-1} with 25 mg L^{-1} gallic acid. Then, the adsorption capacity of the soil for the fungicide was gradually improved with increasing concentration of DOM up to a value of 71.8 mg kg^{-1} with 400 mg L^{-1} gallic acid. Despite the mechanisms involved were not further investigated, the decrease of the solution pH with increasing concentration of gallic acid was hypothesised as the responsible process for enhanced adsorption since imazalil would occur mostly in its cationic form at these conditions.

The adsorption of the herbicide atrazine in a black soil was significantly enhanced in the presence of DOM extracted from the same soil [89]. Cumulative sorption with DOM providing additional sorption sites on soil surface was confirmed as the main mechanism involved in the process. According to Avneri-Katz et al. [100], strongly adsorbed DOM components that are stabilised at the mineral soil surfaces may lead to changes in the affinity of soil surface towards organic pollutants such as pesticides. It appears that DOM impact on polar organic pollutants would be more pronounced at low DOM concentrations due to competition between DOM and polar O-containing pollutants. This phenomenon, however, may be less relevant at higher DOM concentrations as mineral surfaces become less selective towards oxygenated components [100].

Favoured adsorption of atrazine has been found in the rhizosphere zone of a soil previously cultivated with *Pennisetum americanum* [90]. After a spectroscopic analysis of the DOM extracted from soil samples, the increase in atrazine adsorption was justified by the higher binding ability of the DOM derived from the rhizosphere soil, which was richer in lipophilic groups. Therefore, the root exudates altered the adsorption capacity of the soil by modifying the concentration and composition of the DOM in the soil solution, and its binding ability for the pesticide.

Different studies have evaluated the interaction between pesticides and DOM to give some valuable insight into the role of DOM on pesticide adsorption in soils. For instance, the fluorescence characterisation of atrazine–DOM interactions in a black soil [89] revealed that humic-like substances were the main components of DOM and that fluorescence quenching of the humic fraction during atrazine adsorption occurred earlier than other DOM substances, indicating their preferential binding for the herbicide. This is in accordance with a more recent work concerning the binding of atrazine to DOM extracted from soils with different land uses (forest, meadow, cropland and wetland) [101]. These findings suggest that the greater affinity of humic-like molecules for the herbicide controls the overall adsorption process, and that DOM may significantly influence the bioavailability and transport of pesticides irrespective of the land use of soils. Similar effects have been reported for other organic contaminants [102].

Addition of organic amendments, both in solid and liquid form, is a common and smart agricultural and gardening strategy that, as previously described, introduces in soils water-soluble fractions of OM that may interfere in the interaction of pesticides with soil particles (Fig. 1). In a recent study, the strong decrease in the adsorption of glyphosate on different soil domains from macroporous clayey tills by the addition of liquid pig manure extracts was ascribed to both phosphate and DOM in the extracts [91]. This effect was also observed for the more hydrophobic tebuconazole, though less pronounced. Even, tebuconazole adsorption was mainly controlled by soil OC and, therefore, it increased in some soil domains due to the binding of DOM from the manure providing additional sorption sites. By spectrophotometric analyses, two different modes of interactions between glyphosate and DOM fractions were confirmed: while HAs competed with the herbicide for the sorption sites, FAs remained in solution and interacted with glyphosate hence forming stable complexes.

Gaonkar et al. [92] evaluated the effects of DOM extracted from both a mixed waste compost and dried goat organic manure in the adsorption and desorption of dichlorvos and chlorpyrifos on an alluvial soil devoted to wheat and paddy crops. Further, they compared the results obtained with those using commercial HA as a model DOM. Both DOM from organic amendments and HA led to a non-significant increase in the adsorption of the more hydrophilic dichlorvos by providing additional sorption sites, whereas that of chlorpyrifos was substantially reduced. The authors demonstrated that DOM enhanced the solubilisation of the hydrophobic chlorpyrifos, thus promoting its desorption from soil in accordance with previous works [103]. This behaviour was related to the humified and aromatic nature of the DOM under study, which determined the interactions between chlorpyrifos and DOM mainly in the solution, and to a lesser extent in the soil/solution interface. Other studies have also reported the role of DOM from organic amendments on enhancing solubility of medium and low polarity pesticides [15, 104]. In contrast, Calderón et al. [93] reported increased adsorption of oxyfluorfen in a sandy clay loam soil and a silty clay soil after addition of olive-oil mill waste at a 5% rate. Nonetheless, $K_{f\text{-}OC}$ values revealed contrasting effects. While $K_{f\text{-}OC}$ of oxyfluorfen in the sandy clay loam soil decreased after amendment, it was enhanced for the silty clay soil likely due to interactions of DOM with the more abundant clay fraction in this soil, thus providing additional sites in the soil surface for the adsorption of the herbicide. This was confirmed by an increase in soil DOC with respect to the unamended silty clay soil. On the other hand, the higher amount in DOC observed for the sandy clay loam soil after amendment contributed to form stable oxyfluorfen-DOM complexes in solution, thus decreasing the efficacy of the added OM for the adsorption of the pesticide in this soil.

These findings are also in accordance with the work by Thevenot and Dousset [94], who found increased adsorption of diuron in two vineyard soils as a result of amendment with two commercial organic composts (pure vegetal compost and vegetal/animal compost). Nevertheless, this enhancement was significantly lower with the addition of the vegetal compost, which was ascribed to both the large amount of DOM released from the amended soil and the higher contents of carbohydrates and aliphatic carbon of this compost, which favoured interactions in solution of the DOM released with the herbicide.

The use of biochars as soil amendments may also impact pesticide adsorption in soils due to an increase in the amount of DOM in the soil pore water [71, 72]. In this sense, the sorptive capacity of biochars for tricyclazole was negatively related to their DOM content [70]. Similarly, adsorption of the herbicides aminocyclopyrachlor and bentazone on a silt loam soil was increased with the addition of biochars produced from wood pellets, but it was reduced in soils amended with a biochar produced from macadamia nut shells [95]. In contrast, the adsorption of pyraclostrobin, a fungicide highly sorbed to soil, was not modified by biochar addition [95]. Therefore, it is deduced from these works that while the amendment of soil with biochars did not impact the adsorption of less mobile pesticides, biochars with high DOM contents may induce reduced adsorption of highly mobile compounds. Other authors assessed the changes induced in the adsorption of the ionisable herbicides azimsulfuron and penoxsulam in two paddy soils (P100 and P700) by 5% addition of raw and HCl-treated biochar from a by-product of olive oil industry [67]. Adsorption of azimsulfuron increased when P100 soil was amended with raw biochar, but it was reduced for the HCl-washed biochar. In P700 soil, with lower DOC content, adsorption of this herbicide increased regardless of the biochar used. In the case of penoxsulam, adsorption slightly decreased or increased in P100 and P700, respectively, when the soils were amended with both types of biochars. This work concluded that the chemical composition of the water-extractable fraction (including DOM) of the biochar affected the adsorption of azimsulfuron but not that of penoxsulam.

Exogenous DOM from wastewaters may also alter the dynamics of pesticides in soils (Fig. 1). Thus, irrigation of soils with wastewater from olive oil production has been reported to induce some changes in soil composition and properties, such as a reduction of the pH, or an increase in electrical conductivity, water repellency and OM [105]. This accumulation of soil OM as a consequence of repetitive wastewater application resulted in enhanced adsorption of simazine and diuron, which was dependent on the structure of the pesticide itself [97, 105]. However, this increase could not be attributed solely to an increase in soil OM, but also to changes in soil OM nature and sorption mechanisms [96].

In contrast with the aforementioned works, adsorption of dimethenamid and fenarimol [98] or thiacloprid [99] was not significantly affected by short-term irrigation of soils with municipal wastewater. Nevertheless, desorption of the relatively water-soluble herbicide dimethenamid from soils was significantly enhanced [98]. In summary, when DOM concentration was increased up to 300 mg C L^{-1}, a concentration one order of magnitude higher to that normally found in urban wastewaters, adsorption of the more hydrophobic fenarimol increased but that of dimethenamid and thiacloprid was only slightly affected. In the case of fenarimol, co-sorption phenomena were postulated as responsible for increased pesticide adsorption, whereas interactions with DOM in solution seemed to predominate for the less hydrophobic dimethenamid and thiacloprid. In other words, while the DOM molecules adsorbed to soil increase the adsorption of more hydrophobic compounds, the non-retained fraction of DOM may enhance the solubilisation of more polar pesticides, thus increasing the risk of natural waters pollution.

3.2 Leaching

The knowledge of the vertical transport of pesticides through soil is essential to assess the vulnerability of deeper soil layers and groundwater resources to contamination. Pesticide transport depends on pesticide and soil properties, such as surface preparation, soil structure, soil water content, type of irrigation, pesticide structure or pesticide formulation, and the prevailing environmental conditions, such as rainfall events [106, 107]. DOM may facilitate the likelihood of pesticide mobility through soils, because it may decrease adsorption, which is a process inversely related to transport. This section covers studies undertaken either in the field or in the laboratory, the latter normally using disturbed or undisturbed soil columns (Table 2).

The transport of the triazine herbicide atrazine has been the subject of numerous studies. The effects of DOM from rice straw or treated wastewater were studied in laboratory assays (soil columns or soil thin-layer plates) [84, 108]. Apart from indoor experiments, a field assay with this herbicide was also conducted in a plot irrigated for more than 100 years with untreated wastewater [109]. In the laboratory, DOM from both sources promoted the mobility of atrazine and the increase in DOM concentration resulted in both an earlier elution of the atrazine maximum peak concentration and a higher cumulated elution of the pesticide [84, 108]. In the field experiment, the content of DOM and particulate OM of wastewater was suggested to facilitate the transport of atrazine to deep percolation water. Nonetheless, the relatively large volume of water applied to the field (up to 3.5 pore volumes using overflow irrigation), together with the short time elapsed between pesticide application and irrigation, could have masked this effect [109].

Another field experiment, which lasted 2 years, assessed the transport of the pesticides chlorotoluron and flufenacet in an agricultural soil unamended or amended with spent mushroom substrate or green compost [110]. Addition of amendments increased OC in soil down to 50 cm. Consequently, two opposing effects were noticed: on the one hand, the higher soil OC increased pesticide adsorption, especially that of the more hydrophobic flufenacet; secondly, DOM

Table 2 A summary of the effect of DOM from different sources on the transport of pesticides in soil

	Pesticide properties[a]		Soil properties					
Pesticide	Ws (mg L^{-1})	Log Kow	Sand:clay (%)/OC, OM (%)/pH	DOM source	DOC content (mg L^{-1})	Experimental design	Main results	Ref.
Atrazine	35	2.7	31:31/1.3/7.6	Rice straw	60 and 180	• Disturbed soil columns • Soil thin-layer plates	DOM increased pesticide mobility. Earlier pesticide elution at a higher DOM concentration	[84]
Atrazine	35	2.7	15:60/1.3/5.7	Swine WW	1333[d]	• Disturbed soil columns • Sterile and non-sterile soils	DOM increased pesticide mobility in comparison with distilled water	[108]
Atrazine	35	2.7	n.a.:28/2.6/7.1 (0–15 cm) n.a.:40/1.4/7.5 (25–40 cm)	Untreated WW	50	• Field assay • Two soil depths • WW applied for 100 years • Large irrigation volumes	Rapid disappearance of atrazine (degradation + transport). Possible relationship with irrigation volumes and immediate irrigation after pesticide application	[109]
Chlorotoluron Flufenacet	74 51	2.5 3.5	80–68:15–22/0.8–0.3/6.3–7.7 (0–160 cm)	Spent mushroom Green compost	• Spent mushroom, 0.38–0.26[e] • Green compost 0.16–0.14[e]	• Field assay • Soil cores (100 cm) • Two years	OC from amendments increased retention but DOC enhanced mobility even further. Higher effect for spent mushroom, which released more DOM. Pesticide adsorption and degradation parameters should be corrected with the DOC content for a better fitting of the prediction models	[110] [111]

Terbuthylazine	6.6	3.4	92:6/0.78/ 6.5 S1 61:23/0.80/ 8.5 S2 34:44/1.9/ 7.5 S3 70:16/0.18/ 8.0 S4	Olive mill WW	25,000	Disturbed soil columns with sorbed pesticide	Reduction of herbicide leaching with olive mill WW, due to its accumulation in soil pores. Higher effect for S1 and S4, with less clay and OC	[112]
Diuron Imidacloprid	36 610	2.9 0.57	70:13/0.4/ 6.0 S1 14:35/0.9/ 8.2 S2	Two vermicomposts from winery wastes (V1 and V2)	140– 182 V1 79–151 V2	Disturbed soil columns	After amendment, DOC elution increased. Both vermicomposts led to a delay in pesticide elution (higher for diuron) and reduced pesticide leaching, more in S1. Possible DOM adsorption on soil surface	[113]
Diuron	36	2.9	30:34/1.4/ 8.1 S1 67:9/0.5/ 5.6 S2	Three composts (A, B and C)	70 A 33 B 35 C	Intact soil columns	Soil amendments increased extractable OC. Soil type was determinant for diuron transport. While leaching increased in S2, with lower retention capacity, it was even reduced in S1	[94]
MCPA	29,390	−0.81	44:24/0.97/ 6.8 S1 54:14/0.67/ 5.7 S2 43:42/1.3/ 8.2 S3 49:30/0.99/ 7.8 S4	Fresh and aged de-oiled two-phase olive mill waste	Fresh: • 2,000–3,000^{e} (2.5% dose) • 3,800–5300^{e} (5% dose) • 10,200^{e} (10% dose) Aged: • 375–617^{e} (5–10% dose)	• Disturbed soil columns • Fresh and aged amendment	Fresh amendments increased MCPA leaching in S1 and S2 (lower pH), did not modify it in S3 and reduced it in S4. Aged amendments, further reduced MCPA leaching from S4 soil in comparison with fresh wastes. Possible formation of MCPA-DOM complexes in solution	[114]

(continued)

Table 2 (continued)

Pesticide	Pesticide properties[a]		Soil properties	DOM source	DOC content (mg L^{-1})	Experimental design	Main results	Ref.
	Ws (mg L^{-1})	Log Kow	Sand:clay (%)/OC, OM (%)/ pH					
Fenobucarb	420	2.78	7:28/1.8/ 5.1	Spruce forest soil	0, 5 and 25	• Intact soil columns • Flooding under aerobic or anaerobic conditions	Higher DOM release under aerobic conditions, resulting in more pesticide leached. For endosulfan and DDT, DOC concentrations >25 mg L^{-1} are needed for a relevant effect	[115]
Endosulfan	0.32	4.75						
DDT	0.006	6.91						
Thiacloprid	184	1.26	31:11/1.2/ 8.1	• WW • DOM from sewage sludge	3–300	Disturbed soil columns	Leaching of DOM enhanced at high DOC (300 mg L^{-1}). At low DOCs (3–25 mg L^{-1}), low or negligible effect on pesticide transport. At higher DOC, possible co-elution of DOM and thiacloprid	[99]
Cartap	200,000	−0.95	23:11/ 0.69^c/7.5^c S1 9:13/0.79/ 7.1 S2 18:15/0.37/ 6.3 S3 5:19/0.84/ 6.9 S4	• Freshwater • WW	<1^d and 124^d	Disturbed soil columns	WW retarded the leaching of both pesticides. WW increased soil OC, improved soil structure and soil-pore distribution	[116]
Carbendazim	8	1.48						

Isoproturon Epoxiconazole	70 7.1	2.5 3.3	4:31/2.3/7.5	DOM from control soil and from soil amended with compost of sewage sludge and green waste	11.2 and 9.7	• Undisturbed soil cores • Flow interruptions	Faster transport with DOM. No effect for isoproturon, but DOM increased epoxiconazole leaching. Possible competition between DOM and pesticides for sorption sites. No clear effect of DOM origin	[104]
p,p'-DDT *p,p'*-DDE *p,p'*-DDD	1.2–5.5[b] 65 0.009	6.2–6.9[b] 5.7–7.0 6.02	47:21/2.2/8.0 (top 5 cm)	Citric and oxalic acids (mimicking root exudates)	ca. 5,000	• Undisturbed soil columns • Aged pesticide residues	Enhancement of release of *p,p'*-DDT and *p,p'*-DDE. The organic acids break soil organomineral linkages, increasing DOM release, especially enriched in the fulvic acid fraction	[117]
p,p'-DDT *o,p'*-DDT *p,p'*-DDE *o,p'*-DDE α-HCH β-HCH γ-HCH δ-HCH	1.2–5.5[b] 1.2–5.5 65 65 10 5 7.3–17 1	6.2–6.9[b] 6.8 5.7–7.0 6.9 3.8 3.8 3.6–3.7 4.1	n.a.:32/1.1/5.1	Oxalic acid Tartaric acid Citric acid	240 480 720	Disturbed soil columns	HCHs were released from the columns more rapidly than the more hydrophobic DDTs or DDEs. Destruction of soil organomineral linkages by organic acids, releasing entrapped DOM	[118]

Ws water solubility, *Log Kow* octanol/water partition coefficient, *OC/OM* content in organic carbon/matter, *DOC/DOM* dissolved organic carbon/matter, *n.a.* not available, *WW* wastewater

[a] Pesticide properties from PPDB (https://sitem.herts.ac.uk/aeru/ppdb/en/atoz.htm)

[b] Pesticide properties from reference [118]

[c] Soil OC and pH, after irrigation with freshwater

[d] Biological oxygen demand

[e] DOC in mg g^{-1}

from the amendments enhanced the transport of pesticides to deeper soil horizons and their bioavailability to be degraded (especially for chlorotoluron, of intermediate polarity). The latter fact was favoured by a rainfall event shortly after pesticide application. Spent mushroom substrate, which released higher DOM content to the soil solution, could therefore entail a higher potential risk for groundwater contamination than green compost. The same authors [111] used mathematical models for predicting the pesticide fate and called for the inclusion in the leaching models of the formation of pesticide–DOC mobile complexes, in line with repeated claims of other authors [119, 120].

Other researchers have explored the disposal of urban or agricultural wastes to soils, with potential effect of the DOM added on pesticide transport. Aharonov–Nadborny et al. [112] polluted columns of four soils with low OC content with terbuthylazine, and eluted them with olive mill wastewater, a residue from the olive crop industry with very high DOM content. Although they confirmed that terbuthylazine solubility increased with DOM, addition of this wastewater to soil columns resulted in a decreased herbicide leaching from soil. As explained by the authors, the applied solution (rich not only in DOM but also in suspended OM) accumulated on soil pores and enriched soil OM, thus offering new sorption sites for the herbicide. This increased retention was greater in the two soils with lower OC and clay contents (75 and 91% contributions, respectively). Similarly, Fernández-Bayo et al. assessed the leaching of diuron and imidacloprid, together with their metabolites, through two soils amended with two vermicomposts from winery wastes [113]. Vermicompost addition contributed to an enhanced leaching of DOM from the columns. However, addition of both amendments delayed and reduced the leaching of the pesticides and the metabolites, with the effect being greater for diuron than for imidacloprid or the more polar metabolites. The proposed mechanism, coinciding with the above, was DOM adsorption on the soil surface, which would enhance the soil adsorption capacity for pollutants.

The leaching behaviour of diuron was also studied in soil columns prepared from two soils, a clay loam and a sandy loam, amended with three composts with different degrees of maturity [94]. As in the previous study, leaching of DOM increased in the amended soil columns. In the clay loam soil, the addition of composts reduced or did not change diuron transport. However, in the sandy loam soil, with lower capacity for DOM adsorption, a facilitated co-transport of diuron and DOM was observed, increasing the leaching of the herbicide. In addition, the maturity and nature of the composts, which would affect the hydrophilicity of the amendment, were found to be important factors in favouring the presence of diuron in solution.

Peña et al. [114] also added fresh de-oiled two-phase olive mill waste to three Mediterranean soils and a field-aged de-oiled two-phase olive mill waste to a fourth soil. The transport of the highly soluble and ionisable herbicide MCPA in unamended and amended soil columns was investigated. When adding fresh amendments, pH rather than DOM affected herbicide transport, with a more marked reduction of MCPA leaching from the basic soil (S3). Due to the ionisable character of the herbicide, formation of DOM-MCPA complexes in solution would counterbalance MCPA affinity for soil particles, thus explaining the enhanced transport at lower soil pH at which MCPA occurs partially in its neutral form. The addition of aged residue, which released much lower DOM amount, significantly reduced the leaching of MCPA. The different nature of the aged amendment, shown by different HA content or polymerisation grade, among others, could have favoured adsorption of MCPA onto the soil.

Another approach consisted in flooding 25 cm-depth intact soil columns, collected from a paddy field soil, to explore whether aerobic and anaerobic conditions affected the transport of three pesticides [115]. DOM (isolated from a forest soil) enhanced to a different extent the release of fenobucarb, endosulfan and DDT. Under aerobic conditions, DOM concentration in the soil solution was higher, with an important contribution from the soil itself. Therefore, the increase in pesticide leached (2–4 times higher) was the result of both endogenous and exogenous DOM. Nonetheless, an increase of added DOM concentration to 25 mg C L^{-1} was needed for a significant release of the more hydrophobic compounds DDT and endosulfan.

Unlike hydrophobic compounds, the leaching of more polar and/or water-soluble pollutants to environmentally hazardous levels would require much higher DOM concentrations. The amount of thiacloprid leached from a calcareous soil was not modified when using urban wastewater as the influent solution [99]. Similarly, DOM addition at similar concentrations showed low or negligible effect on the transport of polar, and sometimes ionisable, pharmaceutical products [121]. However, DOM solutions extracted from urban sewage sludge yielded a different behaviour. While low concentrations of DOM (3 mg C L^{-1}) reduced the amount of pesticide leached to 38%, infiltration of a 100-fold higher DOM concentration enhanced the amount leached to 55%, closer to that of the control treatment with MQ water (66%) [99]. This was explained by the higher DOM concentration in the leachates at longer pore volumes for the treatment at 300 mg C L^{-1}. At this high DOM concentration, co-elution phenomena of the pesticide with DOM were postulated to occur.

Mojid et al. [116] evaluated the transport of the insecticide cartap and the fungicide carbendazim through columns of soil collected from four Bangladesh areas, watered with freshwater or urban wastewater, which largely differed in DOC. The leaching of both chemicals was retarded when treating the soil columns with wastewater with respect to freshwater. Cartap, highly polar, was less affected and showed retardation factors ranging from 1.18 to 1.25 for freshwater and from 1.24 to 1.29 for wastewater. For carbendazim, with lower polarity, the values were in the ranges 1.28–1.35 and 1.33–1.43, respectively. These findings were related to increased soil OC, reduced soil microporosity, and improved soil pore-size distribution and soil structure when wastewater was infiltrated.

Chabauty et al. [104] examined the effect of DOM at relatively low concentrations on the mobility of four pollutants differing in polarity: two pesticides, isoproturon and epoxiconazole; and two pharmaceutical products, ibuprofen and sulfamethoxazole. DOM was sampled from two sites, one that had received organic amendments for several years and another one from an unamended plot. The effects of DOM depended on the hydrophobic and ionisable character of the pollutants. The more hydrophobic compounds (epoxiconazole and ibuprofen) showed an enhanced transport, while no obvious effects were noted for the more polar compounds (isoproturon and sulfamethoxazole), in line with the previous findings. The underlying mechanism for the hydrophobic compounds would be DOM competition with the pollutants for the same sorption sites, although DOM could also contribute to decreased sorption by interacting with the pollutants in soluble and colloidal phases. No clear effect of the origin of DOM on pesticide fate could be assessed.

Other sources of DOM have been also considered. Plants exude organic compounds through their roots, which consist mainly in LMW organic acids [31, 122]. A mixture of citric and oxalic acids (0.05 M each) enhanced the release of *p,p'*-DDT and *p,p'*-DDE from a column of a loamy soil collected in an area historically polluted with *p,p'*-DDT, *p,p'*-DDE, and *p,p'*-DDD [117]. The influence of the acids on the availability of DDTs was related with the mobilisation of soil OM fractions, especially the more water-soluble FA fraction, because LMW organic acids might promote soil disruption by breaking organomineral linkages. This was confirmed by an increase in OC concentration and electrical conductivity in the leachates after the application of the organic acids. Citric acid, with one hydroxyl and three carboxyl groups, has been reported to be more efficient in pollutant release than oxalic acid, with two carboxyl groups, possibly because it generates a much more stable complex [123].

Liling et al. [118] also evaluated the effect of oxalic, tartaric and citric acids (0.01 M each) on the release rate of various organochlorine pesticides from soil. In the first hours of contact, α-, β- and γ-HCH were released 3 times more rapidly with LMW organic acids than the highly hydrophobic DDTs or DDEs. Several mechanisms were proposed, but dissolution of soil minerals and partial destruction of the soil organo-mineral linkages were put forward as the key processes to explain accelerated release of sorbed pesticides. As above, the ability of citric and tartaric acids, polydentate compounds, to release loosely bound pesticides was greater than that of oxalic acid.

3.3 Degradation

The effects of DOM on pesticide dissipation in soil are usually attributed to two main processes: (a) increase of pesticide availability due to enhanced pesticide solubilisation by DOM and (b) increased degradation due to co-metabolism, because of the enhancement of microbial activity in the presence of more available and easily biodegradable OM [48]. The revised literature shows degradation experiments conducted with soils presenting a wide array of physicochemical properties, and with DOM solutions at varied concentrations and from different sources (Table 3). DOM has been also reported to trigger the photolytic degradation of pesticides in aquatic systems [135]. Nevertheless, these mechanisms could be of importance only on the soil surface exposed to direct sunlight. Therefore, photodegradation of pesticides in soils is not covered in this chapter.

Table 3 A summary of the effect of DOM from different sources on the degradation of pesticides in soil

Pesticide	Pesticide properties[a]		Soil properties	DOM source	DOC content (mg L^{-1})	Experimental design	Main results	Ref.
	Ws (mg L^{-1})	Log Kow	Sand:clay (%)/OC, OM (%)/pH					
Molinate, simazine, isoproturon, atrazine, propanil, dimethoate, pendimethalin, metolachlor, pyriproxyfen, picloram, DDT, endosulfan sulfate, β-BHC (+ 6 PAHs)	0.006–25,900	−1.92-6.91	Silica sand/n.a./n.a.	• Nile river water (NR) • NR + WW1 (ST) • NR + WW2 (OP) • Water-extractable soil OM (WEOM)	4.0–10.6	• Batch reactors • Temperature (20–30°C)	• ST and OP, with higher biodegradable OM, provided higher removal efficiency • Highly hydrophobic pesticides were removed mainly by adsorption • Pesticides with intermediate polarity were more persistent, degraded through co-metabolism • Polar pesticides showed higher degradability	[124]
2,4-D Bentazone Mecoprop 2,6-Dichlorobenzamide (BAM)	24,300 7,112 250,000 1830	−0.82 −0.46 −0.19 0.38	Mainly sand (some clay and peat)/0.95/n.a.	• DOM from natural water • DOM from green compost	10	• Microcosms and undisturbed columns • Aerobic pesticide degradation with enrichment cultures, using sludge as inoculum	Degradation of 2,4-D was promoted by DOM, especially from green compost. Degradation of the rest of pesticides almost unchanged. Importance of pesticide chemical structure	[125]
Benalaxyl	28.6	3.54	23:54/n.a./8.1	• Tap water • Raw WW • Treated WW	0.9–2.1	Monitoring the evolution of individual enantiomers	Treated and, especially, raw WW slowed down the degradation of benalaxyl. Both solutions led to an enantiomerisation from the R- to the S-isomer	[126]

(continued)

Table 3 (continued)

	Pesticide properties[a]		Soil properties					
Pesticide	Ws (mg L^{-1})	Log Kow	Sand:clay (%)/OC, OM (%)/ pH	DOM source	DOC content (mg L^{-1})	Experimental design	Main results	Ref.
Bentazone Boscalid Pyrimethanil	7,112 4.6 110	−0.46 2.96 2.84	Loamy sand/0.83/ 6.1	• Biochar • Digestate • Mixtures of both	1.6–41.6	Treatments differed in DOC and aromaticity ($SUVA_{254}$) but had similar pH values	Biochar retained the pesticides, while digestate accelerated pesticides' degradation, by co-metabolism. Bentazone mineralisation was the highest with 30% digestate	[127]
Thiacloprid Pendimethalin Fenarimol	184 0.33 13.7	1.26 5.4 3.69	31:11/1.2/ 8.1	• WW • DOM from sewage sludge	3–300	Soil incubation at constant temperature	No effect of WW (25 mg C L^{-1}). At higher DOC, degradability of more persistent pesticides was enhanced, coinciding with stimulation of soil biota	[128]
Chlortoluron Isoproturon	74 70.2	2.5 2.5	31:11/1.2/ 8.1 S1 33:40/ 12.6/ 7.8 S2	• WW	25	Soil incubation at constant temperature	WW led to a more rapid pesticide dissipation. The effect was higher for the silt loam soil, with lower OC content	[129]
MCPA	29,390	−0.81	19:17/1.5/ 5.3	• Plant litter (chopped maize leaves and stems, 1:1)	n.a.	Differentiation between soil close to plant litter (5–6 mm) and more distant soil	Near plant litter, mineralisation of MCPA increased, due to enhanced DOM availability and higher microbial activity	[130]

Atrazine, chloridazon, clofibric acid, dimethoate, diuron, pirimicarb, simazine, triclopyr (+ 11 pharmaceuticals and a solvent)	5–25,900	−0.45-2.87	99:0.5/n.a./n.a.	• River water • Hydrophilic fraction • Hydrophobic fraction • Transphilic fraction	4–8	• Soil columns (3–6 weeks) • DOM fractions	At low pesticide load (0.5 μg L^{-1}), no observed effect. At 2 μg L^{-1}, river water and the hydrophilic fraction resulted in higher biodegradation rates. Possible change of OC content or microbial population	[131]
p,p'-DDT	1.2–5.5^{b}	6.2-6.91^{b}	Loamy soil/1.3/5.9	• Chicken manure compost	55–65	• Flooding • Maximum moisture capacity • 60% relative water content	Faster DDT disappearance as compost dose increased, but small differences among treatments. A lag phase, indicated the use of labile DOM first, rather than the pesticide	[132]
Azimsulfuron	1,050	−1.4	43:20/0.9/8.3	• Alperujo, a residue from olive culture	5	• Unflooded (oxic conditions) • Flooded (anoxic conditions)	An increased trend of pesticide dissipation under anoxic-flooded conditions. DOM simultaneously increased, probably by dissolution of Fe oxides	[133]
Atrazine	35	2.7	n.a.:n.a./1.4/6.9	• Silkworm excrement • Biochar from silkworm excrement	80–180	Soil incubation at constant temperature	Lag phase of 28 d (no initial biotic process). Then, amendments retarded atrazine degradation, probably because DOM altered microbial population	[134]

Ws water solubility, *Log Kow* octanol/water partition coefficient, *n.a.* not available, *OC/OM* content in organic carbon/matter, *DOC/DOM* dissolved organic carbon/matter, *WW* wastewater

[a] Pesticide properties from PPDB (https://sitem.herts.ac.uk/aeru/ppdb/en/atoz.htm)

[b] Pesticide properties from reference [118]

The presence of DOM accelerated the dissipation of pollutants in multi-contaminated soils. Abdelrady et al. [124] evaluated the ability of different solutions with low DOC concentrations to remove a mixture of 19 compounds with a wide range of properties (6 PAHs and 13 pesticides) from a sandy soil. A statistically significant effect of the influent OM composition on pollutant removal was observed at 20°C. Some general relationships with the properties of the pollutants could be established: (1) the highly hydrophobic compounds remained mainly adsorbed on the soil; (2) compounds of intermediate polarity exhibited a relatively higher removal efficiency from the influent solutions with higher OM content, possibly by co-metabolism; (3) polar compounds were weakly retained and showed higher degradability. This study emphasises the importance of the structure and chemical properties of pesticides in their dissipation. Similarly, Luo et al. [125] observed different degradation behaviour of the polar pesticides 2,4-D, bentazone and mecoprop, together with BAM, the main metabolite of the herbicide dichlobenil in water samples containing DOM from natural groundwater and green compost. While degradation of 2,4-D was promoted in the presence of DOM, and the highest degradation rate was obtained with DOM from compost, BAM, mecoprop, and bentazone were only minimally affected.

In another study, DOM showed low effects on the degradation of the enantiomeric fungicide benalaxyl in a forest clayey soil irrigated with tap water and with raw and treated wastewater with very low DOM content [126]. The authors paid special attention to the evolution of the enantiomers, because R-benalaxyl exhibits higher anti-fungal activity than the S-enantiomer. The extremely low DOM concentration of the solutions did not affect the degradation of the racemic mixture. However, the less active enantiomer (S) accumulated in soil irrigated with wastewater, showing an enantiomerisation from the R to the S isomer.

In general, the studies have established that addition of higher concentrations of DOM has a greater effect on pollutant degradation. Mukherjee et al. [127] evaluated the dissipation of bentazone, boscalid and pyrimethanil in a sandy soil by adding mixtures of biochar and a digestate obtained from different wastes. The mixtures had similar pH values but differed in DOC content and aromaticity, with the higher values corresponding to 30% digestate. Biochar alone sequestered the pesticides and reduced the compounds' extractability. On the contrary, all the mixtures containing digestate accelerated pesticide mineralisation, although not proportionally to the digestate load. This was explained because DOM provided carbon and energy source for soil microorganisms, favouring co-metabolism. Although the absolute extent of mineralisation induced by 30% digestate was the highest for the polar bentazone, the relative increases in mineralisation were higher for the less polar and less bioavailable boscalid and pyrimethalin (175 and 620%, respectively) than for bentazone (60%).

Rodríguez-Liébana et al. [128] tackled the persistence of thiacloprid, pendimethalin and fenarimol in a calcareous soil incubated with wastewater containing 25 mg C L^{-1}, and with DOM solutions extracted from urban sewage sludge (30 and 300 mg C L^{-1}). The effect of wastewater or DOM at low concentration on pesticide degradation was almost negligible. However, DOM from the sludge added at high concentration enhanced the degradability of more persistent pesticides, like pendimethalin, likely by stimulation of the soil biota at longer incubation times as shown by soil dehydrogenase activity. ElGouzi et al. [129] also applied wastewater to two Mediterranean soils to study the dissipation of the herbicides chlortoluron and isoproturon. Incubation with wastewater always resulted in more rapid pesticide decay, especially for isoproturon and for the soil with lower OC and clay contents. Since sorption to soil was not altered by wastewater, the increased degradation was either explained by the introduction of exogenous microorganisms, able to degrade these pesticides, and/or by microbial co-metabolism likely stimulated by easily metabolisable DOM molecules from the wastewater.

Addition of plant litter to a loamy soil resulted in an enhanced MCPA mineralisation (27% vs 6%), especially in the soil layers closer to the litter addition (up to a 5–6 mm distance) [130]. The authors related the accelerated MCPA dissipation to an increase in available DOM from plant litter in the upper soil layers, which in turn resulted in higher microbial activity as shown by soil respiration and microbial biomass.

Apart from the usual investigations, the effect of other factors has also been explored in the literature. Bertelkamp et al. [131], using a sandy soil column, assessed the effect of watering with four different OM fractions: hydrophilic, hydrophobic, transphilic and river water OM. Pollutants consisted of 11 pharmaceuticals, six herbicides, two insecticides and a solvent, each at 0.5 $\mu g\ L^{-1}$. Possibly due to the low concentration of the added DOM solutions, no significant differences in pollutant biodegradation rates could be found among the different DOM fractions. However, for a fourfold pollutant load (2 $\mu g\ L^{-1}$ each), watering with hydrophilic and river water OM fractions led to higher average pollutant biodegradation rates than the other two fractions. These differences were tentatively attributed to changes in the composition of microbial community and/or OC along the soil column. The biodegradation rates could not be related to either pollutant hydrophobicity or charge at the pH of the experiments.

Deng et al. [132] examined the influence of three soil moisture conditions on the dissipation of *p,p'*-DDT in a loam soil amended with chicken manure compost at 1–3%. The insecticide disappeared more rapidly with higher compost addition, but differences were small among doses and moisture levels. In all cases, pesticide degradation showed a lag phase of approximately 21 d coinciding with an initial DOM decline. Soil microorganisms may have preferentially consumed first the more labile DOM from compost before using the pesticide as an energy and C source.

The influence of flooding, and therefore, anoxic conditions, on the dissipation of azimsulfuron was also evaluated in a soil devoted to rice cultivation to which was added alperujo, a residue from the olive culture [133]. Under anoxic-flooded conditions, addition of the amendment significantly enhanced DOM concentration in comparison with amended soil under oxic unflooded conditions (twice as high) or unamended soil (5–7 times higher). The anoxic-flooded conditions would reductively dissolve Fe oxides, thus enhancing the release of DOM and, consequently, the dissipation rate of azimsulfuron possibly because of higher pesticide bioavailability.

While there is general agreement that the addition of DOM increases pesticide bioavailability for degradation, few studies report otherwise. This is the case of the research undertaken by Huang et al. [134] who explored the dissipation of atrazine in an agricultural soil after addition of silkworm excrement and its corresponding biochar. As in the previous DDT study [132] a lag phase of 28 d occurred, showing that atrazine did not initially undergo biotic degradation. Afterwards, both amendments retarded atrazine decay, especially the silkworm excrement that provided the highest DOC amount to the soil solution. The degradation delay was explained because the organic amendments altered the relative abundance of bacteria and fungi involved in atrazine degradation, although the formation of bound residues cannot be ruled out.

3.4 *Crop Uptake*

Pesticides present in soil may affect not only target and non-target plants but also other living organisms [136]. However, the literature search from 2015 about how DOM could modulate the effect of pesticides on living organisms has given rise to some results in aqueous solutions but not in soil [137–140]. Therefore, this section has focused on crops grown in soils, from which they can incorporate pesticides (Table 4). This process may also be mediated by the presence of DOM in the soil, especially under those conditions that influence pesticide bioavailability.

The content of atrazine in maize roots and shoots was reduced when plants were watered with DOM solutions obtained from rice straw and diminished when DOM concentration increased from 80 to 160 mg C L^{-1}. The formation of atrazine-DOM complexes would have reduced the passage from the cellular plasma membrane to the root cells because they were too polar or too large in size [84].

Similarly, the concentrations of thiacloprid and fenarimol in tomato shoots were lower when irrigating a mining soil with wastewater in comparison with distilled water [141]. The same research group had reported a decrease in the uptake of both pesticides by ryegrass in another mine soil [142]. Other organic compounds with a wide range of physicochemical properties have shown a similar behaviour [146, 147]. In accordance with the above explanations, wastewater irrigation would have favoured the permanence of both pesticides in the soil solution by formation of pesticide–DOM complexes. An alternative explanation could be a higher pesticide retention in the rhizosphere soil facilitated by DOM, as reported for atrazine and *P. americanum* [90].

The behaviour of isoproturon and chlorpyrifos in wheat [143, 144] and of thiamethoxam, hymexazol and chlorantraniliprole in cucumber seedlings [145] was examined after treatments with salicylic acid, either in the leaves or in the soil. In all cases, this treatment enhanced pesticide decay in soil and reduced pesticide accumulation in plant tissues. Salicylic acid altered plant growth and activities of antioxidant enzymes due to the stress produced by the pesticides. Lu et al. [143] hypothesised that pesticide disappearance in soil was probably boosted

Table 4 A summary of the effect of DOM from different sources on the uptake of pesticides by plants grown in soil

Pesticide	Pesticide properties[b]		Soil properties	DOM source	DOC content (mg L^{-1})	Experimental design	Plant species	Main effect	Ref.
	Ws (mg L^{-1})	Log Kow	Sand:clay (%)/OC, OM (%)/ pH						
Atrazine	35	2.7	31:31/1.3/ 7.6	Rice straw	60 and 180	Soil irrigated with DOM solutions	Maize	Reduction of atrazine in shoots and roots. Possible formation of DOM-pesticide complexes, too large or too polar, to traverse plant cells	[84]
Thiacloprid Fenarimol	184 14	1.3 3.7	8:28/0.23/ 8.2 S1 Sandy loam/1.4/ 2.4 S2	Wastewater	25	Mine soils irrigated with wastewater	Tomato (S1) Ryegrass (S2)	Lower pesticide concentration in plant shoots. Formation of pesticide-DOM complexes in soil solution	[141] [142]
Isoproturon	70	2.5	n.a./2.1/ 7.6	Salicylic acid	5	Spray with salicylic acid once a day for 6 d	Wheat	Spraying with salicylic acid reduced the concentration of the pesticide in wheat, due to promoted pesticide decay. It enhanced the exudation of organic acids (malic, oxalic and, especially, tartaric) and improved soil microbial population	[143]
Chlorpyrifos	1.1	4.7	20:37/n.a./ 6.5	Salicylic acid	1, 2, 4, 8 and 16	Spray with salicylic acid once a day for 6 d	Wheat	Salicylic acid decreased pesticide concentration in root and shoot in comparison with the control. Greater decrease at the lowest concentration (1 mg L^{-1})	[144]

(continued)

Table 4 (continued)

Pesticide	Pesticide properties[b]		Soil properties	DOM source	DOC content (mg L^{-1})	Experimental design	Plant species	Main effect	Ref.
	Ws (mg L^{-1})	Log Kow	Sand:clay (%)/OC, OM (%)/pH						
Thiamethoxam Hymexazol Chlorantraniliprole	4,100 65,100 0.88	−0.13 0.3 2.86	n.a./2/7.0	Salicylic acid	1[a]	Salicylic acid added to the soil. Pot experiments and hydroponic culture	Cucumber	Increased degradation of the pesticides in soil and decreased pesticide concentrations in roots and leaves with salicylic acid. Results explained by promotion of pesticide dissipation (soil microorganisms) or regulation of the plant mechanisms for stress	[145]

Ws water solubility, *Log Kow* octanol/water partition coefficient, *OC/OM* content in organic carbon/matter, *DOC/DOM* dissolved organic carbon/matter, *n.a.* not available

[a] DOC in mg g^{-1}

[b] Pesticide properties from PPDB (https://sitem.herts.ac.uk/aeru/ppdb/en/atoz.htm)

by increased exudation of LMW organic acids that would activate soil biota. After spraying with salicylic acid they detected tartaric, malic and oxalic acids in roots and in different soil fractions, which would have provided the necessary nutrition and energy source for survival and proliferation of rhizosphere microbes, with higher proportion of fungus that are responsible for pesticide degradation.

4 Concluding Remarks

The different studies included in this chapter show that DOM affects the mechanisms that control the fate of pesticides in soil at different extents depending on the properties of pesticides and soils and DOM composition and concentration.

Pesticide adsorption and leaching will therefore depend on the specific interactions among the pesticide, soil particles and DOM molecules. In general, it is accepted that interactions between DOM and pesticides in solution (enhanced pesticide solubility) as well as competition of DOM for sorption sites in the soil surface will contribute to reduced sorption and, consequently, higher availability of the solute to undergo transformation or transport within the soil environment. In contrast, other processes such as cumulative sorption and DOM-pesticide co-sorption will be responsible for an enhancement in the retention of the contaminants.

In recent years, researchers have deployed different strategies in an attempt to better characterise which parts of DOM (fractions, functional groups) are specifically involved in the interactions with pesticides and to unravel the mechanism(s) of interaction DOM–soil–pesticide. Hydrophobic fractions of DOM bind preferentially to the soil surface, resulting in enhanced desorption, solubilisation or leaching, or else allow co-adsorption of pesticides with the bound DOM, thus increasing their retention. More hydrophilic DOM fractions, with high content in FA, favour pesticide solubilisation and decrease adsorption. The hydrophilic/lipophilic ratio of each DOM source can be the cause of the inconsistent results reported in literature. Moreover, the use of amendments or irrigation water with high content of suspended OM may block soil pores, enriching soil OM and hindering the transport of pesticides.

The type of soil has also a bearing on pesticide fate. In soils with low DOM adsorption capacity, such as sandy soils, DOM–soil interactions are low and therefore, the adsorption of a pesticide in soil would be only slightly affected or preferentially reduced by the formation of pesticide-DOM complexes that remain in solution. The opposite occurs for soils with higher ability for DOM sorption, such as clayey soils or soils with high content of Fe/Al oxides.

In general, the higher the DOM concentrations, the higher the effects on pesticide fate. However, it has been repeatedly shown that hydrophobic pesticides usually respond to lower DOM concentrations, while higher concentrations are needed for a significant effect on a polar pesticide to occur. In addition, polar and non-polar pesticides may have different adsorption mechanisms. Hydrophobic partition especially with aromatic DOM moieties would prevail as a mechanism of interaction of non-polar pesticides. On the contrary, computational models suggest that polar organic compounds prefer binding to the hydrophilic domains of humic substances, through H-bonding with specific functional groups (i.e., carboxyl groups). For ionisable pesticides, controversial results have been observed, due to the changes in the soil pH induced by exogenous DOM that in turn may lead to variations in the surface charge of soils.

DOM addition favours microbial enrichment and, therefore, speeds up pesticide degradation by co-metabolism and/or by increasing pesticide concentration in the soil solution. In contrast, it may also induce retardation in pesticide decay in some soil environments since the microbial population may preferentially degrade the labile DOM added. Assimilation of pesticides by plants appears to be reduced in the presence of DOM. The main mechanism exposed to interpret this behaviour is the association of DOM with pesticide in the soil solution, rendering it less available for plant uptake by the formation of pesticide–DOM complexes, either unable to traverse the membrane of root cells or with high transport potential to deeper soil layers.

Our understanding of DOM chemistry and its influence on pesticide–soil interactions deserve further studies with extended application of specific techniques such as FTIR, NMR or fluorescence spectroscopy. Given the differences in the properties of DOM, pesticides and soils presented in this chapter, it is evident that drawing general conclusions concerning the management of polluted soils is challenging. However, considering the important role of DOM on adsorption/desorption, which is a main process governing the transport of pesticides outside its application area, future efforts should be focused on including DOM concentration and properties in the leaching and transport models to predict more accurately the movement of pesticides in soils and thus, their potential impacts to ground and surface waters.

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Assessing the Effects of Pesticides on the Soil Microbial Community: Advances, Standardization of Methods and the Need for a New Regulatory Framework

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Contents

Abstract Upon their application pesticides end up in soil where they interact with the soil microbial community. Considering the pivotal role of soil microorganisms in ecosystem homeostasis and the growing evidence about their potential toxicity response to pesticide exposure, there is an urgent need to revisit the relevant regulatory framework. This is necessary in light of the enormous methodological and standardization advances in soil microbial ecology in the last 20 years and the outdated assessment scheme currently in place. In this chapter we highlight the key elements of a new risk assessment scheme including (a) the definition of microbial

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indicator groups like ammonia-oxidizing microorganisms and arbuscular mycorrhizal fungi (b) the parallel determination of the level and the duration of the exposure including transformation products (c) the need for implementation in environmental risk analysis of advanced and standardized tools. Based on all these a new tiered-risk assessment scheme is proposed. Emerging issues in soil microbial ecotoxicology are discussed including (a) the assessment of pesticide soil microbial toxicity at ecosystem level and (b) the assessment of the soil microbial toxicity of biopesticides, pesticide mixtures and pesticide transformation products on soil microorganisms. We conclude by highlighting emerging scientific questions that are expected to puzzle the soil microbial ecotoxicologists working with pesticides in the next decade.

Keywords Ammonia-oxidizing microorganisms, Arbuscular mycorrhizal fungi, Microbial ecotoxicity, Pesticides, Risk assessment, Soil microbial community

1 Introduction

Pesticides are still the cornerstone of pest control in modern agriculture. However the focus of the pesticide market has shifted in the last 20 years from high dose–low potency chemicals, like triazines and organophosphates, to low dose–high potency active ingredients like neonicotinoids and sulfonylureas. This change coincided, at EU level and beyond, with the implementation of a stringent regulatory framework for pesticide registration reflecting the growing concern of the general public about the frequent detection of pesticide residual levels in fresh produce [1], natural water resources [2, 3] and soil [4]. This regulatory framework was built around the hallmark EC Directive 91/414 (available at https://eur-lex.europa.eu/legal-content/en/ALL/?uri=CELEX% 3A31991L0414), which describes the tests and procedures required for placing in the market a plant protection product (PPP). This was supplemented by (1) the water framework directive (2000/60/EC, available at https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX: 32000L0060), which identified several pesticides as priority water pollutants and (2) the EC Directive 128/2009 (available at https://eur-lex.europa.eu/legal-content/EN/ALL/?uri=CELEX%3A32009L0128), which put into force procedures for the sustainable use of pesticides. Eventually, in 2009 91/414/EC was replaced by the EC Regulation 1107/2009 (available at https://eur-lex.europa.eu/ legal-content/EN/ TXT/?uri=celex%3A32009R1107), which now dictates how a PPP is granted authorization for use in the EU market.

Environmental risk assessment is based on a direct comparison between environmental exposure, determined by mathematical models fed with experimentally obtained environmental fate data, and ecotoxicological outputs derived from relevant studies. This assessment is performed along tiers of increasing complexity and reduced conservatism, which determine the potential risk associated with the use of the given pesticide for the suggested use [5].

Aquatic and terrestrial ecotoxicology were pioneers in establishing a robust set of standardized methods to assess the toxicity of pesticides on macroorganisms. In contrast the potential toxicity of pesticides on soil microorganisms has been overlooked. Soil microorganisms are known as the growth engines of terrestrial ecosystems by (1) controlling several key reactions in nutrient cycling which modulate soil fertility and the production of greenhouse gases (GHG) [6], (2) interacting with crops with the outcome being often beneficial [7] (3) supporting soil structure [8] and (4) providing a wealth of functional biodiversity which could be exploited by biotechnology. In support of all these, the European Food Safety Authority (EFSA) highlighted the presence of regulatory gaps in the assessment of the toxicity of pesticides on soil microorganisms and identified soil microbes as a specific protection goal [9]. Still the assessment of the toxicity of pesticides on soil microorganisms is based on an outdated, crude and insensitive N mineralization test (OECD 216), which offers a lumped measurement of ammonification and nitrification rate in soil.

Hence there is an urgent need for revisiting the current framework regarding pesticides toxicity on soil microorganisms, especially in light of the major methodological advances that have occurred in soil microbiology in the last 15 years. In accordance with this, EFSA issued a scientific opinion [10] acknowledging the need for revising the relevant regulatory framework and suggested that (1) the N mineralization test is still inclusive and should be maintained for pesticide testing (2) new molecular and biochemical tools are available but not yet standardized, hence not ready to be implemented in environmental risk assessment (3) functional microbial endpoints are more easily quantified compared to microbial diversity and (4) arbuscular mycorrhizal fungi (AMF) are good potential bioindicators for assessing the soil microbial toxicity of pesticides. In this review we will (1) define the key elements of a comprehensive assessment of the toxicity of pesticides on soil microorganisms (2) provide an update on the current knowledge regarding toxicity of pesticides on soil microorganisms, the methodological toolbox that is available and the level of its standardization and (3) highlight emerging research questions that should be the focus of future research in soil microbial ecotoxicology. Finally we conclude with our suggestion for a tiered risk assessment approach that could act as a core in the foreseen revision of the current regulatory framework regarding the toxicity of pesticides on soil microorganisms.

2 Key Elements of an Accurate Assessment of the Toxicity of Pesticides on Soil Microorganisms

The assessment of the toxicity of pesticides on the soil microbial community will require a list of necessary elements as follows:

- A thorough and detailed determination of the level and the duration of the exposure of the soil microbial community to the studied pesticides
- The utilization of advanced, high resolution methods which will be adequately standardized to determine with high accuracy the toxicity of pesticides on soil microorganisms
- The selection of appropriate endpoints and soil microbial groups that could act as bioindicators of the toxicity of pesticides to soil microorganisms
- A relevant tiered risk assessment scheme supported by guidelines for experimental setup at each tier

We will further present an update on each of these key elements and define which pieces of the puzzle are still missing.

2.1 Pesticide Exposure Measurement

Monitoring of pesticide dissipation and transformation in soil studies should constitute an integral part of any experiment aiming to assess the toxicity of pesticides on soil organisms, including soil microbiota. Such measurements enable us to define the level and the duration of exposure of the soil microbial community to the pesticide in question. Furthermore, determination of the transformation products (TPs) formed in soil during pesticide dissipation could clarify the role of TPs on effects observed. Correlation testing between the measured soil concentrations of pesticides and their TPs with temporal microbial measurements would point to the causal agent of the potential toxicity on the soil microbial community (parent vs TPs). Using such an approach Karas et al. [11] identified two demethylated products of the herbicide isoproturon, MD-IPU and DD-IPU, as key drivers of the reduced activity of acid and alkaline phosphatases in soils treated with various dose rates of isoproturon. Using a similar approach other research groups managed to distinguish the toxicity of (1) iprodione and 3,5-dichloroaniline [12] (2) tebuconazole and its TPs [13] (3) chlorpyrifos and trichloropyridinol [11].

2.2 Use of Advanced, High Resolution and Standardized Methods

Methodological advances in soil microbiology have revolutionized our view of soil microorganisms and their role in ecosystem functioning. The new molecular tools that became available from 1995 onwards unravelled an enormous microbial diversity in soil ecosystems, which was previously unattained due to our limited knowledge of their special nutritional needs [14]. The molecular and biochemical methods that are currently available could be categorized into two broad groups: (a) *functional tools* that measure either the activity of key microbial processes or the dynamics of functional microbial groups and (b) *structural tools* that measure the diversity of the overall soil microbial community and its phylogenetically or functionally distinct components.

Standardization of methods constitutes a prerequisite for their implementation in pesticide environmental risk analysis. As EFSA suggested [10], standardization of functional methods in soil microbial ecology is more advanced compared to molecular tools for measuring microbial diversity. Biochemical tools measuring the rates of microbially-mediated reactions (e.g. nitrification, denitrification), the overall microbial activity (e.g. respiration) or the activity of microbial enzymes involved in biogeochemical cycling (phosphatases, arylsulfatases, aminopeptidases, chitinases, etc.) have been extensively used for assessing the toxicity of pesticides on soil microbial functioning [11, 12, 15–17]. These methods are characterized by high standardization level with several relevant ISO standards being available (Table 1). In addition, several of these methods, like the determination of activity of soil microbial exoenzymes [18] and soil microbial respiration through MicroResp® [19], have been modified for high-throughput use facilitating their implementation in rapid toxicity screening assays. Despite their high level of standardization these methods are still not used in pesticide environmental risk assessment. A possible reason for this is the general lack of consistency in their response to pesticide exposure. This has been demonstrated in a range of soil studies where pesticides applied at increasing dose rates did not impose a clear dose-dependent response [11, 20].

Molecular methods have been used in soil microbial ecology to determine the abundance (q-PCR), activity (RT-q-PCR) and diversity (PCR-based techniques) of soil microorganisms. The implementation of these methods in pesticide environmental risk analysis was until recently blocked by the lack of standardization [21]. This has changed in the last 10 years where ISO standards for soil DNA extraction (ISO11063) and determination of the soil microbial biomass via q-PCR (ISO 17601) were introduced, challenging the recent scientific opinion of EFSA regarding the low level of standardization of molecular methods [10]. Indeed several soil studies have used q-PCR methods to determine the effects of pesticides on the abundance of phylogenetical distinct microbial groups like bacteria, fungi or archaea or most importantly the abundance of functional microbial groups like ammonia-oxidizing microorganisms (AOM) [22–24], sulphur-oxidizing bacteria [11] and degraders of biogenic aromatic compounds [13].

Several tools are currently available for the determination of microbial diversity in soil, which vary in their level of standardization and phylogenetic resolution. Phospholipid Fatty Acid analysis (PLFAs) is a well-standardized method (ISO/TS29843-1 and -2), which provides information about the composition of the soil microbial community at low phylogenetic resolution. On the other hand, PCR-based molecular methods suffer from limited standardization, but they provide a deeper phylogenetic characterization of the composition of the soil microbial community. The depth of analysis of the soil microbial community offered by these methods has increased from the lower resolution of earlier fingerprinting methods like Denaturating Gradient Gel Electrophoresis (DGGE) and Terminal

Table 1 A list of the ISO standardized methods that are currently available in soil microbiology

Year	ISO code	Full title of standardized method
1997	ISO14240:1	Determination of soil microbial biomass – part 1 substrate induced respiration method
1997	ISO14240:2	Determination of soil microbial biomass – part 2 fumigation-extraction method
2002	ISO16072	Laboratory methods for determination of microbial soil respiration
2009	ISO10832	Effects of pollutants on mycorrhizal fungi- germination test
2010	ISO/TS29843-1	Determination of soil microbial diversity – part 1: Method by phospholipid fatty acid analysis (PLFA) and phospholipid ether lipids (PLEL) analysis
2011	ISO/TS29843-2	Determination of soil microbial diversity – part 2: Method by phospholipid fatty acid analysis (PLFA) using the simple PLFA extraction method
2012	ISO15685	Determination of potential nitrification and inhibition of nitrification – rapid test by ammonium oxidation
2012	ISO14238	Determination of nitrogen mineralization and nitrification in soils and the influence of chemicals on these processes
2012	ISO17155	Determination of abundance and activity of soil microflora using respiration curves
2016	ISO17601	Estimation of abundance of selected microbial gene sequences by quantitative PCR from DNA directly extracted from soil
2016	ISO18187	Contact test for solid samples using the dehydrogenase activity of *Arthrobacter globiformis*
2018	ISO/TS20131-1	Easy laboratory assessments of soil denitrification, a process source of N_2O emissions – part 1: Soil denitrifying enzymes activities
2018	ISO/TS20131-2	Easy laboratory assessments of soil denitrification, a process source of N_2O emissions – part 2: Assessment of the capacity of soils to reduce N_2O
2018	ISO20130	Measurement of enzyme activity patterns in soil samples using colorimetric substrates in micro-well plates
2019	ISO23753:1 ISO23753:1/AMD1:2020	Determination of dehydrogenase activity in soils – part 1: method using triphenyltetrazolium chloride (TTC) Determination of dehydrogenases activity in soils – part 1: Method using triphenyltetrazolium chloride (TTC) – Amendment 1
2019	ISO23753:2 ISO23753:2/AMD1:2020	Determination of dehydrogenase activity in soils – part 2: method using iodotetrazolium chloride Determination of dehydrogenase activity in soils – part 2: method using iodotetrazolium chloride – amendment 2
2019	ISO/TS22939	Measurement of enzyme activity patterns in soil samples using fluorogenic substrates in micro-well plates
2020	ISO11063	Method to directly extract DNA from soil samples

Restriction Fragment Length Polymorphism (TRFLP) [25, 26], to the higher resolution of recent next generation amplicon sequencing approaches or the so-called metataxonomics [27]. DGGE and TRFP, either as stand-alone approaches or in combination with clone libraries, have been heavily used in the period of 2000–2015 to determine effects of pesticides on the diversity of phylogenetically and functionally distinct microbial groups [28–31]. However these methods fail to provide accurate quantitative information on pesticide effects, especially on less abundant members of the soil microbiota. Since 2015 several studies have used metataxonomic approaches to identify effects of pesticides on the diversity of bacteria, fungi [32, 33] and distinct functional microbial groups like ammonia-oxidizing microorganisms (AOM) [12]. Benchmarking protocols for the preparation and setup of metataxonomic analysis of the soil bacterial (https://earthmicrobiome.org/protocols-and-standards/16s/) and fungal diversity (https://earthmicrobiome.org/protocols-and-standards/its) were developed by the Earth Microbiome Project (ECM) [34] and have been largely adopted by most recent pesticide soil ecotoxicity studies. Despite this major standardization step, we are still missing standardization at the bioinformatic handling of the sequencing data. A standardized pipeline for the bioinformatic analysis of amplicon sequencing data will make possible the full implementation of these powerful tools in the pesticide regulatory framework.

2.3 Microbial Endpoints and Bioindicators

Assessment of the toxicity of pesticides on aquatic organisms but also on terrestrial macrobiota relies on tests performed with single species from different trophic levels identified as bioindicators. Such examples are *Daphnia magna* for aquatic invertebrates, *Oncorhynchus mykiss* for fishes and *Eisenia fetida* for earthworms [10, 35]. All these bioindicator species were selected based on (1) their key ecological role (2) their higher sensitivity, compared to other species in the same group of organisms (3) their meaningful ecotoxicological response to toxicants (4) our good knowledge of their life cycle and (5) the existence of assays, protocols and methods to determine their response to pesticides. In accordance with all these, we need to identify microbial groups which fulfil all or most of the above criteria as candidate bioindicators for assessing the toxicity of pesticides on soil microorganisms.

Several groups of soil microorganisms have been proposed or used such as microbial indicators including AOM [36], AMF [10, 23], N-fixing bacteria [37], protists [38] and microalgae [39]. Most studies have focused on the first two microbial groups, in line with their key functional role in terrestrial ecosystems, although protists have also attracted attention in recent years due to their important role as mediators of bacterial and fungal populations in soils [40].

AOM control the rate-limiting step of nitrification, the energy-gain oxidation of ammonia to hydroxylamine which is further transformed to nitric oxide and eventually to nitrite [41]. Nitrite is subsequently oxidized to nitrate by nitrite-oxidizing bacteria (NOB) [42] (Fig. 1). Nitrification constitutes one of the most important inputs of N in soil contributing 330 Tg of N per year [43], hence perturbations in its operation are expected to adversely affect N balance in soil. Beyond nitrification, AOM have been found to contribute to N_2O emissions, a major GHG, through a process called nitrifiers denitrification [44]. Ammonia oxidation constitutes a specialized process controlled by (1) ammonia-oxidizing bacteria (AOB), mostly

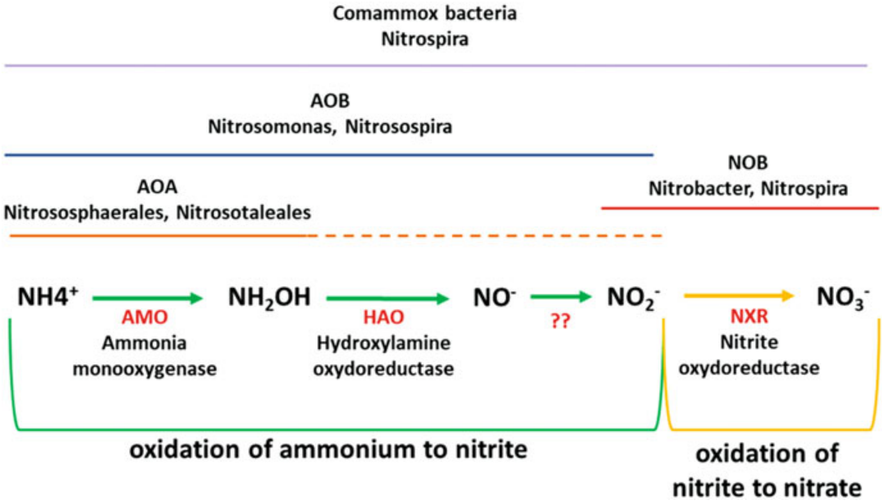

Fig. 1 A schematic representation of the microbially mediated transformation of nitrogen during nitrification along with the groups involved in each step of the process. *AOA* Ammonia oxidizing archaea, *AOB* Ammonia oxidizing bacteria, *NOB* Nitrite oxidizing bacteria, *Comammox* Complete ammonia oxidation bacteria

belonging to β-proteobacteria and specifically to *Nitrosomonas* and *Nitrosospira* [45] (2) ammonia-oxidizing archaea (AOA) belonging to the phylum Thaumarchaeota with lineages Nitrososphaerales and Nitrosotaleales dominating in soil ecosystems [46] and (3) comammox bacteria which perform the full nitrification process in one cell [47] and was recently shown to actively participate in ammonia oxidation in soil [48]. The contribution of the different groups of AOM in ammonia oxidation in soil is largely determined by soil physicochemical attributes like pH [49] and ammonia concentrations pointing to an AOM niche specialization [50, 51]. All AOM share an enzyme called ammonia monooxygenase, a periplasmic enzyme which is responsible for the oxidation of ammonia to hydroxylamine [43]. The gene encoding the alpha subunit of ammonia monooxygenase (*amoA*) provides a thorough phylogenetic classification of AOM [45, 46]. This gene constitutes the key marker gene for the design of group-specific primers for AOA, AOB and comammox bacteria [52–54] that have been used in q-PCR, RT-q-PCR and amplicon sequencing to determine the abundance, activity and diversity of AOM in soil ecosystems [12, 20].

The responsiveness of nitrifiers to pesticides was first reported by Domsch [55] who observed a high sensitivity of *Nitrosomonas* and *Nitrobacter* to pesticides. Since then, further studies reinforced the sensitivity of AOM to abiotic stressors and suggested their use as microbial bioindicators [36]. Indeed, several studies have explored the response of AOM to pesticide exposure by measuring their abundance via q-PCR [24, 56–58], their activity via measurements of potential ammonia oxidation (or potential nitrification) [20], and their diversity via DGGE, TRFLP or amplicon sequencing of the *amoA* gene [12, 31, 59]. Recent studies by Hund-Rinke et al. [60] tested the toxicity of silver nanoparticles, as potential pesticides, on soil microorganisms using a range of standardized methods including potential nitrification (or so-called potential ammonia-oxidation method ISO 15685), MicroResp®, and exoenzymes activity. The former was the most sensitive endpoint providing a consistent dose-effect response allowing the calculation of EC_{50} values. Similar studies have also reported the sensitivity of potential nitrification to pesticide exposure [20, 61]. Potential nitrification is a measure of the rate of the microbial transformation of ammonia to nitrite, in contrast to the N-mineralization test which is a lump measurement of ammonification and nitrification compromising its sensitivity to abiotic stressors. All the above evidence along with its ISO standardization (ISO 15685) reinforce its potential for implementation in the battery of tests that could be used to assess the toxicity of pesticides on soil microorganisms.

Most studies to date have tested the effect of different pesticides to AOM abundance via q-PCR of the *amoA* gene, but only a few have worked at transcription level. In one of these few studies, Papadopoulou et al. [20] observed a clear temporal inhibition of the activity of AOM in soil by ethoxyquin only when *amoA* transcripts were measured. Considering the high turnover rates of RNA in soil, RNA-based approaches are expected to provide a more accurate view of the effects of pesticides on the activity of functional microbial groups like AOM. However, the labile nature of RNA has precluded its wider use in pesticide microbial ecotox studies and maybe its use could be considered when refinement of the ecotox part of the risk assessment is requested. Overall AOM constitute good potential bioindicators for the assessment of the toxicity of pesticides on soil microorganisms since (1) they control a very significant function in soil N cycling (2) they are particularly sensitive to pesticide exposure providing a consistent and relevant ecotoxicological response (3) we have a good knowledge of their life cycle, ecology, biochemistry and physiology and (4) we have well-standardized methods to measure their activity and abundance in an accurate way.

Apart from AOM other N-cycling microbial groups have been considered as valuable toxicity endpoints including denitrifying bacteria [62] and N-fixing bacteria [37]. Pesticide effects on denitrification has been measured through q-PCR analysis of bacterial genes involved in the different steps of denitrification, although results were contrasting and no clear ecotoxicological response was seen [11, 62, 63]. Pesticide effects on N-fixing bacteria have been also investigated, mostly via *nifH*-based q-PCR, with the results varying from no inhibition by trifluralin (especially compared to AOM) [64], to temporal inhibition by chlorothalonil [65] and to strong inhibition by 1,3-dichloropropene [66].

AMF were identified as potential bioindicators for assessing the toxicity of pesticides on soil microorganisms [10, 16]. AMF are the most ubiquitous plant symbiotic microbes on earth with up to 80% of plants colonized by obligate biotrophic fungi of the phylum Glomeromycota [67]. They colonize roots and derive plant photosynthates in exchange for nutrients (up to 80% of plant P is of AMF origin), offering plant tolerance to biotic and abiotic stress [68]. Besides improving plant fitness, AMF also contribute to the formation and stabilization of soil aggregation [69] and improve soil carbon stocks [70]. At the ecosystem level AMF could affect the composition and productivity of plant communities with reciprocal effects on nutrient cycling [71].

AMF sensitivity to pesticides has been extensively studied at various experimental scales [16, 72, 73]. However, their obligatory symbiotic nature and their biological cycle which involves intraradical and extraradical life stages require the use of complementary experimental approaches to identify the nature of the inhibitory effects observed: direct on AMF or indirect stemming from phytotoxicity effects on the plant host. Direct effects on AMF are expected to be imposed mostly by fungicides, unlike herbicides whose effects on AMF are expected to be indirect by exerting their toxicity to the plant host. In addition, the different life stages of AMF are not expected to be equally exposed to pesticides, while the consequences of pesticide exposure for AMF survival are expected to vary in the different life stages. Extraradical AMF life stages are more prone to pesticide exposure, unlike intraradical stages which are less exposed. The standard ISO-10832 «Effects of pollutants on mycorrhizal fungi- germination test» could be used to assess effects of pesticides on extraradical stages of AMF, using spore germination of *Funneliformis mosseae* as a relevant toxicity endpoint. Giovanneti et al. [74] tested the effect of 14 pesticides on spore germination and pre-symbiotic mycelial growth and observed that fungicides were more toxic than the other pesticide groups tested. Mallman et al. [75] proposed an optimization of the ISO test with the use of *Gigaspora albida* and *Rhizophagus clarus*, to cover a wider diversity of AMF, and boric acid as negative control instead of cadmium nitrate.

Pot and field studies have been also employed to assess the toxicity of pesticides on natural assemblages of AMF. In those studies, plant roots mycorrhizal colonization, P content and other plant physiological attributes (root and shoot biomass) are often used as ecotoxicological endpoints to identify potential adverse effects on AMF [72, 76]. These plant-soil studies introduce realism and complexity in ecotoxicological assessment, but at the same their outcome is affected by several confounding pesticide- and AMF-related factors. A classic example is provided by the study of Karpouzas et al. [16] which showed that nicosulfuron when applied repeatedly in soil at rates higher than x10 the recommended dose rate led to a dramatic decrease in maize roots colonization by AMF, although it was not possible to distinguish if effects were direct on AMF or indirect driven by plant host phytotoxicity. The use of in vitro tests with AMF could complement pot studies and provide a conservative estimate of the potential toxicity of pesticides on the different life stages of AMF, and hence clarify the nature of the effects observed.

In vitro cultivation of AMF is possible on self-propagating mycorrhized Ri tDNA-transformed roots of *Daucus carota* or *Medicago truncatula* growing in sterilized minimal medium [77, 78]. These mono-compartmental axenic culture systems have been used to assess the toxicity of pesticides at the symbiotic phase and allow the calculation of IC_{50} values. Wan et al. [77] calculated the IC_{50} values for a range of pesticides using reduction in extraradical mycelium sporulation as the most conservative endpoint. Benomyl, chlorothalonil and glyphosate were the most toxic pesticides with IC_{50} values <1 mg/L compared to AMPA ($IC_{50} = 4.2$ mg/L), the major transformation product of glyphosate, and the biopesticide azadirachtin (IC_{50} = 230 mg/L). Subsequently, Zocco et al. [79] used a modified bi-compartmental system composed of a root compartment (RC) and hyphae compartment (HC) to test the toxicity of fenpropimorph and fenhexamid on the symbiotic phase, the hyphae and the spores at the post-symbiotic phase and also on the root biomass. A three-compartment AM-P system composed of a shoot compartment (SC) where a plantlet shoot grows, and the RC and SC described above were proposed by Dupré de Boulois et al. [80]. AM-P systems have been used to test the toxicity of pesticides like fenpropimorph and fenhexamid on the capacity of extraradical hyphae and spores to colonize roots, while it offers the opportunity to determine effects on P uptake using ^{33}P [78]. These AM-P systems could be further advanced including a second SC associated with the HC to systematically test the effect of pesticides on the capacity of extraradical hyphae to sporulate and colonize plant crops where the pesticide tested is destined for use [73]. Besides just determining toxicity endpoint values for AMF, these in vitro cultivation systems could be used for the determination of the toxicity mechanism, the nature of the effect observed, and also of potential effects on the physiology of symbiosis. Campagnac et al. [81] used the single compartment axenic culture system to determine the effects of fenhexamid and fenpropimorph on the sterol biosynthesis in mycorrhized plantlets. Zocco et al. [78] used the AM-P system to define the toxicity mechanism of the same two fungicides focusing on plant P uptake machinery.

The introduction of molecular tools in the study of AMF unravelled an enormous diversity which revolutionized the taxonomy of Glomeromycota [82]. Still only a few studies have looked into the effects of pesticides on the diversity of AMF. Karpouzas et al. [16] using a DGGE – cloning approach showed that nicosulfuron, when applied at rates multiple times higher than the recommended, could result in a dramatic decrease in the diversity of AMF in maize roots. Rivera-Becerril et al. [83] studied the effect of a mixture of fenhexamid, folpet and deltamethrin applied at x1, x10 and x20 dose rates on the soil diversity of AMF, via clone library with taxon-specific primers and observed a reduction of AMF soil diversity with increasing dose rates. Jin et al. [76] constitutes the only study to date that used amplicon sequencing to determine the effects of a range of pesticides on AMF intraradical diversity. They observed pesticide-specific effects on AMF community with *Gigaspora hoi* and *Acalauspora uera* showing increasing sensitivity to fludioxonil in pea and chickpea, respectively.

Overall, AMF appear to be also good candidate bioindicators to assess the toxicity of pesticides on soil microorganisms since (1) they control a series of key functions in soil ecosystems (2) we have standardized tools to define effects of pesticides on their growth (3) we have a good knowledge of their life cycle and biology and (4) they are generally sensitive to pesticides. However, we should note that due to their symbiotic nature a combination of in vitro and soil-plant studies are often required in order to define the true extent of pesticides toxicity on AMF.

2.4 Tiered-Risk Assessment Scheme and Standardization of Experimental Planning

To date environmental risk assessment of pesticides relies on a tiered system starting from simple and highly conservative Tier I assays and moving gradually to less conservative and more realistic Tiers II and III. To date no such risk assessment scheme is available for soil microorganisms. Pioneering studies by Jonhen and Drew [84] and Atlas et al. [15] proposed for the first time a set of experimental procedures and rules on how to determine the toxicity of pesticides on soil microorganisms. Both studies agreed that if significant inhibitory effects on soil microbial functioning are observed at lab scale, the toxicity of pesticides on soil microorganisms should be further examined at field tests. Following the same philosophy, Karpouzas et al. [23] established a two-tiered risk assessment procedure where lab soil microcosms are employed at Tier I to determine the toxicity of pesticides on soil microorganisms. If effects are observed a Tier II assessment at field scale should be undertaken (Fig. 2a). Subsequently Karpouzas et al. [85] provided a more conclusive tiered system composed of three tiers of increasing experimental complexity based on the ecotoxicological response of key soil functional groups like AOM and AMF (Fig. 2b). This scheme is composed of (1) a Tier I highly conservative in vitro screening of pesticides against a set of soil derived AOM and AMF strains that cover the different ecophysiological and phylogenetic variants of these microbial groups (2) a Tier II toxicity assessment in lab soil microcosms (or pot studies when AMF are considered) against natural assemblages of AOM and AMF and (3) a Tier III toxicity assessment at field scale against natural assemblages of AOM and AMF. In case where an unacceptable risk for soil microorganisms is still evident refinement of exposure could be an option to minimize risk. Fast track in vitro tests for AOM and AMF are available and have been used in the past to assess pesticides toxicity [12, 73, 78]. However certain aspects of these tests should be standardized (e.g. selection of the most ecotoxicological relevant strains for testing) before considered for inclusion in the regulatory framework.

Several studies have assessed the toxicity of pesticides on soil microbial diversity or functioning. However inconsistencies in experimental planning have prevented the systematic characterization of the potential risk associated with the use of pesticides for soil microorganisms. Below we will identify the most common problems in experimental planning and we will propose certain solutions for a more systematic and thorough determination of the soil microbial toxicity of pesticides.

- In most ecotox studies pesticides are applied at increasing dose rates and the effects on selected endpoints are followed. Several studies have used particularly high pesticides levels, up to x100 and x1000 the recommended dose rates or application schemes that are not relevant to the registered application scheme of the tested pesticide [23, 28, 86]. Effects observed under these experimental conditions are not ecotoxicologically relevant and do not substantiate a potential

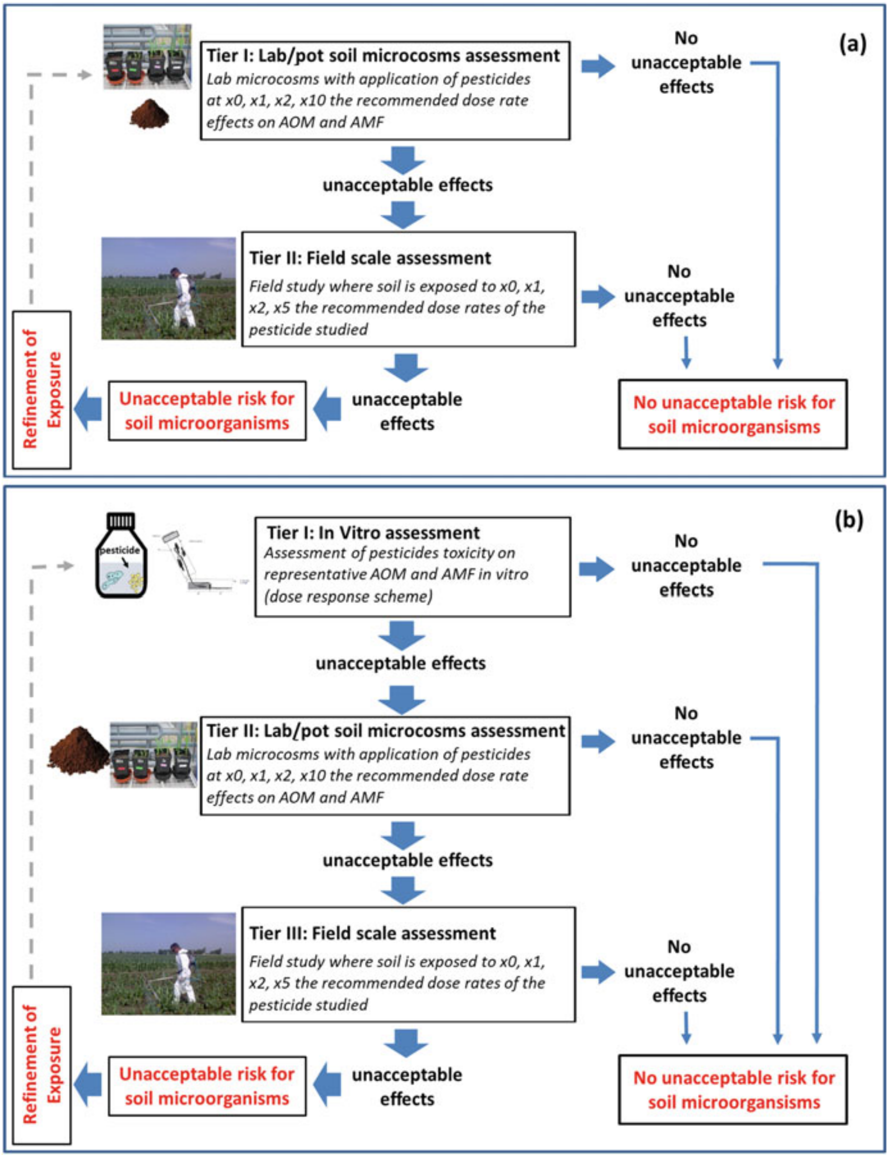

Fig. 2 Two-tier risk assessment (**a**) and three-tier risk assessment schemes (**b**) proposed for assessing the risk associated with the use of pesticides for soil microorganisms. *AOM* Ammonia-oxidizing microorganisms, *AMF* Arbuscular mycorrhizal fungi

risk for soil microorganisms. We propose (1) in lab tests pesticides will be tested at x1, x2 and x10 the recommended dose rate and (2) in field tests pesticides will be tested at x1, x2 and x5 the recommended dose rate (3) at both experimental scales a non-treated control treatment should be included.

- Several soil studies investigating the effects of pesticides on soil microorganisms are often of limited duration (e.g. 30 days). This does not allow a potential recovery of the soil microbial community from temporal effects that might be evident at the first 30 days of exposure. We propose that (1) soil lab tests will be extended to at least 70 days depending on the persistence of the pesticide tested, and temporal measurements of microbial toxicity endpoints will be performed along the experimental duration (2) field tests should be extended for the whole growing season of the crop used. Such a monitoring setup will allow potential recovery to be observed.
- Several of the currently available studies have explored the effects of pesticides on selected functional and diversity microbial endpoints in a single soil limiting the applicability of the results. We propose that all lab tests to be performed at three soils with varying pH and organic carbon content, two parameters that are known to affect pesticide behaviour [87] but also microbial activity and diversity [6].
- When summarizing studies looking at the effects of pesticides on AOM we noted that only a few of them have considered amending soil with ammonium prior to pesticide exposure [12, 22, 59]. This practice is essential to trigger the proliferation and activity of AOM in soil. However due care should be taken regarding the source (inorganic or organic) and the level of ammonium added in the soil. Both of these parameters are known to strongly affect the activity of the different microbial players in ammonia oxidation in soil [50].
- A final tip that we believe it is essential for studies focusing on the effects of pesticides on AMF is the inclusion of plant species which are relevant for the agronomic use of the tested pesticides.

3 Emerging Issues in the Assessment of the Soil Microbial Toxicity of Pesticides

A new risk assessment scheme for defining in a robust way the potential risk for soil microorganisms due to pesticide application is urgently required. The use of the tiered risk assessment scheme proposed here, combined with the use of AOM and AMF as bioindicators of the toxicity of pesticides on soil microorganisms and the implementation of advanced and standardized tools would fill the gap in pesticide regulatory process. The initial focus on functional microbial endpoints could further expand to diversity endpoints when the on-going standardization of modern metataxonomic tools will be finalized. Still there are emerging issues regarding the study of the toxicity of pesticides on soil microorganisms that should be the focus of studies in the next few years. Some of these emerging issues are described in the following paragraphs.

3.1 Toxicity of Pesticides at Soil Ecosystem Level

Most studies to date have assessed the toxicity of pesticides on individual taxa or functional groups separately or in the context of a specific biochemical pathway ignoring the ecological dimension of the effects observed. However, in soil microorganisms are assembled in subpopulations which are intertwined by metabolic links or other types of interactions and can be important for ecosystem homeostasis [88, 89]. Resilience and robustness of microbial consortia to external perturbations has been attributed either to microbial diversity, which enables tolerant members to fill functional voids left by intolerant species [90], or to functional complementarity of network members resulting in better exploitation of resources and elevated resistance to stress [91]. Little is known about the impact of pesticides on soil microbial networks and the consequences for soil functioning. A functional microbial network that could be utilized in such an approach could be AOM, NOB and denitrifying bacteria. Previous studies have looked into the effect of pesticides in the above functional microbial network via gene abundance measurements which provided conflicting results [11, 65]. Measurements at activity level (RT-q-PCR) and determination of the concentrations of N intermediates supporting a metabolic flux analysis would provide a robust assessment of the potential toxicity of pesticides on soil microbial networks.

Microorganisms also interact with other organisms within the soil-food web. Predator–prey relations are particularly important for soil ecosystem functioning with protists-bacteria being the best-studied model system [92]. Predation by protists influences bacterial and fungal diversity and productivity with consequences on the flux organic nutrients into biomass at higher trophic levels [93, 94]. Recent studies showed that the diversity of both protists and bacteria interactively determines the performance of the predator [95]. External perturbations like the application of pesticides could affect diversity at both trophic levels with possible effects on ecosystem functioning [96, 97]. To date research on the impact of pesticides has overlooked potential effects on multiple levels in soil food webs and microbial interactions. The protists–bacteria relationship could be used as a model predator–prey system in a soil-food web centric assessment of the toxicity of pesticides on soil microbiota. This could be determined in simple synthetic microbial communities (quasi in vitro systems) and further to complex natural soil assemblages enabled by the major advancements in microbial diversity analysis at both trophic levels [98].

3.2 Toxicity of Pesticide Mixtures and Co-formulants

PPP contain, apart from the active ingredient, several co-formulants that ensure that maximum pesticide amount will reach the target. The identity of these co-formulants is rarely known but they seem to contribute partially or heavily to the toxicity of pesticides on soil microorganisms. The potential effects of co-formulants on the soil microbiota could be experimentally addressed via a comparative assessment of effects triggered by the pure active ingredient and the corresponding commercial formulation. This is a practice that is not largely followed when assessing the toxicity of pesticides on soil microorganisms through the OECD 216 test. In such a comparative study, Crouzet et al. [99] showed that the commercial formulation of the herbicide mesotrione when applied at x10 or x100 the recommended dose induced stronger effects on the structure of soil cyanobacteria compared to the pure active ingredient. Similarly, Rousidou et al. [31] demonstrated that glucose and skimmed milk powder, contained as additives in a commercial formulation of the nematode parasitic fungus *Paecilomyces lilacinus,* were responsible for a temporal inhibition of AOM upon soil application of the commercial formulation BIOACT®.

Besides additives, PPP commonly contain more than one active substance (ca. 25% in Germany) [100], hence releasing mixtures of pesticides in the environment that may exhibit effects deviating from those seen when applied individually. Studies have explored the aquatic toxicity of such mixtures [101] and suggested that for mixtures composed of pesticides with the same or different mode of action the concentration addition (CA) or the independent action (IA) models, respectively, could predict toxicity [102]. In contrast, little is known about the toxicity of pesticide mixtures on soil ecosystems. Evaluating the applicability of CA and IA models for assessing the soil microbial toxicity of pesticides or devising new models, more relevant for soil ecosystems, could be a new frontier in pesticide soil microbial ecotoxicology.

3.3 Toxicity of Biopesticides

The growing public concern about the effects of synthetic pesticides on environmental quality and soil health has shifted attention to biopesticides which have gained ground in the pesticide market. Biopesticides is a broad group of pesticides of biological origin which could be broadly categorized to (a) microbials where the active agent is a microorganism that protect crops from fungal and insect infestations (b) natural products or biochemicals or botanicals that are biogenic compounds, products of the secondary metabolism of plants and microorganisms with strong biocidal activity. Due to their biological origin, biopesticides are a priori considered as low risk. However this remains to be verified by a number of specific studies. The most studied natural product regarding its off-target toxicity to soil microorganisms is azadirachtin, with the results obtained being not in support of a low-risk profile. In vitro tests suggested low risk of azadirachtin for AMF [77]. However soil studies showed that azadirachtin even at the recommended dose had a consistent inhibitory effect on the abundance and the transcriptional activity of AOM, N-fixing bacteria and denitrifying bacteria [56, 103] and negatively affected the diversity of bacteria, fungi and AMF [30, 57]. In fact the effects observed were equal or even higher than those induced by comparatively studied synthetic pesticides. An interesting study by Romdhane et al. [104] compared the effects of the natural triketone herbicide leptospermone and its synthetic derivative sulcotrione on the soil microbial community. In line with the results of azadirachtin they noted that leptospermone induced a stronger perturbation on the soil bacterial community compared with its synthetic counterpart. These studies certainly challenge the general perception that natural products are characterized by lower off-target toxicity compared to synthetic pesticides.

Even less studies are available for microbial pesticides. Potential toxicity effects of microbials on the soil microbial community largely depend on the mode of action of the microbial pesticide itself. Hence microbial pesticides based on microorganisms which do not act through the production of biocidal compounds are not generally expected to affect soil microorganisms. This was clearly the case for the nematode parasitic fungi *P. lilacinus* strain PL251 which did not have a direct inhibitory effect on AOM [31]. In contrast Yu et al. [105] using a different *P. lilacinus* strain PL1210 showed strong inhibitory effects on nitrification and AOM abundance which were attributed to antimicrobial metabolites that the tested strain produces. Other relevant studies also suggested that microbial pesticides based on microorganisms acting through parasitism or antagonism (i.e. *Metarhizium brunneum, Fusarium oxysporum f.sp. stringae, Bacillus amyloliquefaciens*) did not appear to induce strong and persistent effects on the soil microbial community [106–108].

According to the registration framework in Europe biopesticides are collectively treated as low-risk compounds, still undergoing the same registration process as synthetic pesticides. Although this could be relevant for natural pesticides, we argue that the risk assessment procedure for microbial pesticides should be adjusted to account for the particularities of these products. This should certainly include parallel ecotoxicity tests between formulations and active microbial agents along with the implementation of tools for monitoring their fate in soil.

3.4 Toxicity of Transformation Products

In addition to parent compounds, pesticide environmental risk assessment extends to their TPs that are formed at levels >10% of the parent compound. Minor TPs (<10% of the parent compound) could evade risk assessment, although they might exhibit similar or even higher toxicity than the parent pesticide if they carry toxicophore moieties in their structure [109]. Several studies have showed that TPs could be more toxic than the parent compound. For example, Papadopoulou et al. [20] showed that quinone imine, a TP of ethoxyquin used as preservative in fruit packaging plants, was responsible for the inhibition of AOM in soils treated with ethoxyquin. Further studies by Vasileiadis et al. [12] suggested that 3,5-dichloroaniline, a major TP of iprodione, was responsible for the strong inhibition in the abundance and activity of AOM in soils treated with iprodione. Similar soil studies with chlorothalonil showed that the formation of 4-hydroxy-chlorothalonil resulted in strong inhibitory effects on microbial activity [110]. Advances in analytical chemistry have enabled the detection of previously unknown TPs formed even in low concentrations [111]. Recently, enviPath, a database and prediction tool for the biotransformation of organic contaminants [112], has been updated with all freely accessible EU regulatory data on pesticide degradation in lab soil studies with the aim to develop more accurate prediction for pesticide biotransformation pathways [113]. Complementary tools (i.e., QSAR) enabling the prediction of the soil microbial toxicity of TPs could allow for a targeted investigation of the TPs toxicity.

4 Conclusions and Future Perspectives

The assessment of the soil microbial toxicity of pesticides constitutes a major gap in the current pesticide regulatory framework and corrective actions are urgently required. These should encompass the dramatic methodological advances in soil microbiology and their increasing level of standardization. In this quest we believe that key functional microbial groups like AOM and AMF should have a key role as bioindicators of the toxicity of pesticides on soil microorganisms. This short list of microbial indicators should be gradually enriched with other potential candidates like protists or other microbial groups that could be identified through the use of advanced ecotoxicological tools (i.e. Species Sensitivity Distributions) in a meta-analysis of high-throughput amplicon sequencing data. This will be facilitated by the development of a database of amplicon sequencing data derived from studies investigating the toxicity of pesticides on the soil microbial diversity. A first example of such an effort is the microbiome stress project presented by Roca et al. [114].

Function-based toxicity endpoints are more mature and standardized for immediate implementation in the regulatory process unlike diversity endpoints whose standardization is still on-going. Furthermore, we still lack a clear scientific evidence-based answer to the question "How much soil microbial diversity loss we could accept without compromising soil ecosystem functioning". Studies providing evidence for decision making at this level will open the route for the implementation of microbial diversity endpoints in pesticide ecotoxicity assessment.

We are currently at the era of amplicon sequencing approaches which provide a high-resolution overview of the phylogenetic composition of the soil microbial community and of the response of its individual members to pesticide exposure. However, this approach could not provide any information about the functional role of the affected microbes which requires metaomic approaches. The introduction of metagenomic and most importantly metatranscriptomic analysis in studies looking at the effects of pesticides on soil microorganisms would provide a holistic view of the functional response of the soil microbial community to pesticide exposure identifying key responders and toxicity mechanisms.

Up to date literature evidence suggests that pesticides when used at the recommended dose rates are not expected to impose adverse effects on the soil microbial community. Still a concerted action is required to be able to identify exceptions to this statement and this could be achieved through the establishment of a robust scheme of toxicity and risk assessment analysis.

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Environmental Fate of Chiral Pesticides in Soils

Beatriz Gámiz, Rocío López-Cabeza, Lucía Cox, and Rafael Celis

Contents

Abstract Chirality has received progressive attention in the field of pesticides. Enantiomers of chiral pesticides have identical physicochemical properties but, commonly, they exhibit stereoselective response with chiral host systems and, therefore, enantioselectivity against the target pest. Despite this, approximately 30% of the pesticides in current use are formulated as mixtures of enantiomers or racemic mixtures. This has engendered new environmental problems, which demand exhaustive knowledge regarding the enantioselectivity of the processes that chiral pesticides may undergo in the soil environment. Changes in the enantiomer composition of chiral pesticides are caused mainly by biological interactions and, consequently, factors affecting the biodegradation of pesticides can also alter the

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enantioselectivity of the biotransformation of chiral pesticides in soils. Accordingly, soil parameters such as pH, redox conditions, texture, or agronomic practices have been reported to indirectly influence the final enantioselective behavior of these pesticides in soils, although there is limited knowledge in this regard. Hence, predicting the environmental behavior of chiral pesticides in soil turns challenging. This chapter summarizes the most recent enantioselective studies on chiral pesticide transfer and transformation processes in soils. Future research needs scientific foundations to establish under which agricultural and environmental conditions it is appropriate to replace racemic chiral pesticide mixtures with the biologically active purified enantiomers, the underlying mechanisms of enantioselective interactions, and the relationships between the soil microbial diversity and the biotransformation of chiral pesticides, which remain largely unknown.

Keywords Chiral signature, Enantiomeric fraction, Enantiomers, Enantioselective behavior, Enantioselective degradation, Soil

1 Introduction

The search for new agrochemicals with higher specificity and efficiency for the control of weeds and pests in crops has led to the development of pesticides with increasingly complex structures, many of them chiral [1, 2]. Chiral pesticides have at least one asymmetric center in their structure that results in two enantiomeric forms (optical isomers or enantiomers), which are non-superimposable mirror images of each other [1]. Usually, the asymmetric or chiral center is a carbon atom attached to four different substituents, although chirality can also arise from the presence of asymmetric phosphorus or sulfur atoms [3] (Fig. 1).

The most accepted system to name the configuration of an asymmetric center is the Cahn-Ingold-Prelog convention that assigns a letter R or S to each center depending on the spatial distribution of its substituents. If this absolute configuration is unknown, then (+) and (−) prefixes, according to their interaction with plane-polarized light, can be used to name the enantiomers [4]. It should be noted that there is no universal relationship between the absolute configuration (R or S) and the direction (+ or −) in which the enantiomers rotate plane-polarized light, which can even change depending on the solvent used [5].

Unlike other types of stereoisomers, the enantiomers of a chiral compound have identical physicochemical properties in achiral environments. Nevertheless, enantiomers may differ in their behavior in chiral environments, either in the presence of a physical chiral medium, such as the plane-polarized light, or a chemical chiral one, such as solvents, reagents, or catalyzers [6, 7]. The soil offers a great chiral medium due to the presence of microorganisms, enzymes, and other chiral constituents. Thus, the behavior and fate of the enantiomers of a chiral pesticide in soil can differ, since the transfer and transformation processes that chiral pesticides undergo in soil may be enantioselective. To assess the enantioselectivity of these processes, the

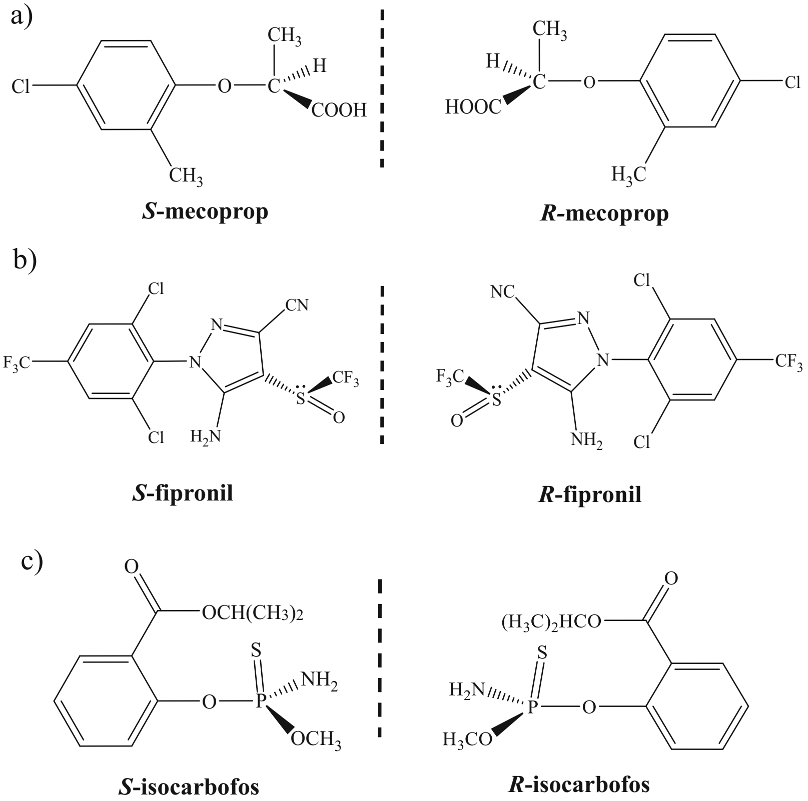


Fig. 1 Examples of chiral pesticides whose asymmetric centers are C (**a**), S (**b**), and P (**c**) atoms

abundance of one enantiomer (E1) is compared with the other (E2) by determining the enantiomeric fraction, and its changes, according to the expression $EF = E1/(E1 + E2)$. EF values range from 0 to 1, with $EF = 0.5$ representing a racemic mixture and $EF \neq 0.5$ representing the predominance of one enantiomer over the other [8].

Many studies have reported that the effect of enantiomers on target and non-target organisms is usually different [9]. In most cases, only one of the enantiomers (active enantiomer) of a chiral pesticide is responsible for the biological activity against the target pest, as the molecular objective of the pesticide is usually an enzyme or a biological receptor whose active center is also chiral [10]. On the other hand, the behavior and final fate of inactive enantiomers are usually unknown. Consequently, the application of racemic mixtures of pesticides implies the addition of a substance without real functionality that could overload the self-recovery capacity of soils and affect non-target organisms. Therefore, the application of pure enantiomer formulations of chiral pesticides to fields is a green practice to consider in pest control [7]. Among the benefits of using the active enantiomer over the racemic mixture, besides reduction of environmental damage and ecological risk, is the reduction of

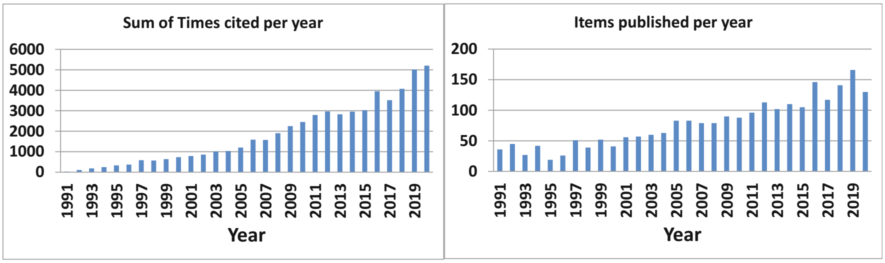


Fig. 2 Items published and sum of times cited to them on chiral pesticides per year. Source: ISI Web of Knowledge, Web of Science-Citation Report, April 2021. Search criteria: "chiral" and "pesticide"

application doses [3, 7], which means an increase in the profitability and the safety of the pesticide applicator. However, it is estimated that pesticide formulations consisting of pure enantiomers represent only 7% of the current pesticide market [11, 12]. This predominance in the use of racemic mixtures is in part due to the expenses associated with the production and/or purification processes, which makes their commercialization less profitable [2, 12]. However, currently, several methods are available to prepare chiral pesticides with sufficient efficiency to be produced at an industrial scale [2, 7].

The first studies about the enantioselective behavior of chiral pesticides go back to the 90's decade, although the interest in this kind of compounds has increased in recent years due to the unique environmental consequences associated with their use (Fig. 2). Currently, the application of chiral pesticides for pest control in the agro-industry is widespread all over the world [7]. It is estimated that approximately 30% of the active ingredients registered nowadays are commercialized as racemic mixtures of the enantiomers of these pesticides [2, 13, 14] and that more than 40% of the insecticides and herbicides used in China are chiral [9]. In addition, since 2015, a great development of chiral pesticides has been observed, a trend that seems to carry on [2].

The authorities have been more aware of the necessity of performing exhaustive studies on the possible enantioselectivity in the behavior and final fate of chiral pesticides in the environment, and even of recommending, in some cases, the use of the pure active enantiomer [15]. In fact, based on the different bioactivity of the enantiomers, several countries have taken action. For instance, the Dutch and Swiss authorities revoked the licenses for the use of racemic mixtures of chiral phenoxyalkanoic acids while the registration of products with the pure active isomer was approved. Another example is Sweden, where a tax as a function of the weight of chiral active ingredient was implemented [9]. Moreover, at the European level, regulation No. 1107/2009 [16] requires specifying the identity and content of isomers/diastereoisomers of the newly registered plant protection products and classifies those that contain a significant proportion of inactive isomers as candidate substances to be substituted. Based on this regulation and at the request of the European Commission, the European Food Safety Agency (EFSA) developed an

EFSA guidance on risk assessments for active substances in plant protection products that contain stereoisomers as components or impurities, or for transformation products of active substances which may have stereoisomers [17]. In the case of the USA, the Environmental Protection Agency (EPA) has issued an interim policy on the reevaluation of chiral pesticides for their replacement by pure enantiomers [18]. These international authorities (EFSA and EPA) have pointed out the lack of information on the stereoisomer-specific behavior of chiral active substances and have expressed their concern on how this ignorance could affect their risk assessment. For this reason, an exhaustive evaluation of the possible enantioselective behavior of chiral pesticides in soils is crucial. In this chapter, recent findings on the enantioselectivity of the main transfer and transformation processes to which pesticides are subjected in soil and their implications on the effects of chiral pesticides on target and non-target organisms are summarized.

2 Sorption of Chiral Pesticides in Soils

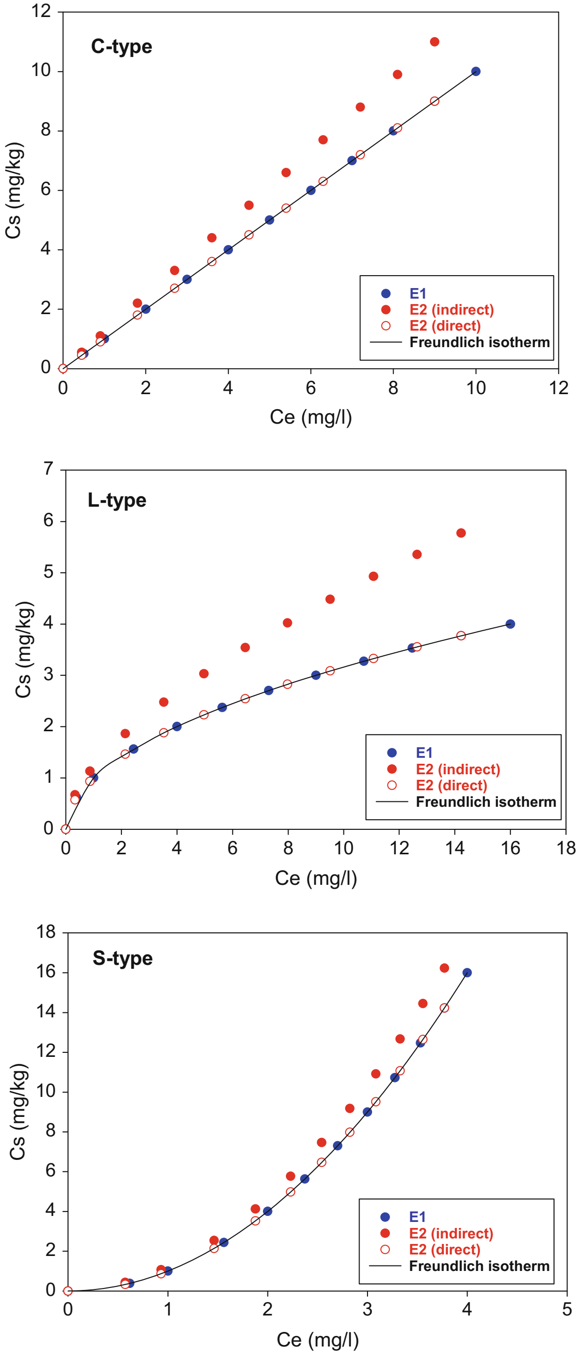
Sorption is a key process dictating the final fate of pesticides in soils, since it reduces the fraction of the pesticide available to be transported to deeper soil layers or to be degraded, while desorption causes the opposite effect. Because of the identical physicochemical properties of enantiomers, it is generally assumed that abiotic environmental processes, including sorption, are non-enantioselective [19]. If enantioselective soil sorption took place, other soil processes, such as leaching, runoff, or volatilization, would be altered, with the subsequent contribution to the prevalence of one enantiomer over the other in the various environmental compartments (e.g., soil, water, and air samples).

Sorption enantioselectivity requires the existence of a chiral soil environment, which is presumed possible since soils present chiral minerals and organic matter chiral regions with the potential of changing the chiral signatures of pesticide residues [20]. This link, however, has not been unequivocally proven, and the demonstration of the occurrence of enantioselective sorption in natural soils is still challenging [21–23]. Several reasons can explain the apparent difficulty to obtain such evidence. Achiral soil surfaces, for example, can be more abundant than chiral ones and hamper the observation of enantioselective sorption, which is difficult to observe under conventional batch sorption experiments [21, 22]. Furthermore, although different chiral sorption sites in soil may indeed be enantiomer-selective and cause enantioselective sorption at the local or microscale, because of the heterogeneity of soils, differences may be compensated at the global scale, resulting in an apparent lack of enantioselectivity [22, 23]. Hence, when sorption is measured by batch equilibration procedures at the macroscopic level, it is not projected that the interactions between the soil components and chiral pesticides in the soil solution are selective enough to discriminate between enantiomers [17, 21]. In this line, many studies have observed lack of sorption enantioselectivity in soils for chiral pesticides such as metalaxyl [24–28], benalaxyl and furalaxyl [29], tebuconazole [30], imazaquin [31], as well as for chiral natural compounds with the potential to be used as biopesticides, such as abscisic acid [32, 33] or carvone [34, 35]. Some of these studies also found that the lack of enantioselectivity remained after soil modification with different types of inorganic and organic amendments [26–28, 31, 35].

A less studied situation occurs when the chiral pesticide exists in the soil in a non-racemic form. This situation can arise when a particular chiral pesticide is applied as an enantiomer-enriched active ingredient or because of enantioselective biodegradation, as will be discussed in the next section. An enantiomer-enriched solution implies that the initial EF value of the pesticide differs from 0.5. In this regard, some investigations have aimed to establish whether enantioselective sorption can occur in soils from non-racemic pesticide enantiomer mixtures [36]. Hall [36] compared the sorption of racemic metalaxyl and metalaxyl-M (the R-enantiomer-enriched product of the fungicide metalaxyl) on bentonite and montmorillonite. Her experiments revealed that sorption of R-metalaxyl was higher than that of racemic metalaxyl on both sorbents, and it was proposed that enantioselective sorption of R-metalaxyl could have occurred. Subsequent investigations performed by Celis et al. [21] attempted to get additional insight into the possibility of the occurrence of enantioselective sorption of metalaxyl in soil using racemic and non-racemic initial solutions. The authors found that metalaxyl sorption in soil occurred enantioselectively when initial aqueous solutions enriched in R-enantiomer were used. Considering the shape of the sorption isotherms (S-type), it was proposed that metalaxyl solutions enriched in R-enantiomer could have induced an enantioselective sorption behavior whereby the R-metalaxyl enantiomer was preferentially sorbed over the S-enantiomer, probably at soil clay mineral surfaces, due to homochiral R-R interactions in the sorbed state being more favorable than heterochiral R-S interactions. This effect would lead to greater sorption of metalaxyl-M (R-enriched) compared to racemic metalaxyl (R + S) [21]. In addition, the mechanism was considered compatible with the absence of enantioselectivity observed for the sorption of metalaxyl in soil from racemic initial solutions and with previously reported differences between racemic metalaxyl and metalaxyl-M in their sorption to mineral samples [36].

An important experimental artifact that can influence the identification of the sorption enantioselectivity may arise from the preferential biodegradation of one enantiomer over the other during the sorption measurement. In the traditional batch equilibration technique, the amount of compound sorbed is commonly determined by calculating the difference between the amount initially added and that remaining in solution after equilibration. Consequently, the preferential biodegradation of one enantiomer over the other during the sorption measurement could be erroneously interpreted as enantioselective sorption. The relevance of this artifact is illustrated in Fig. 3, which represents the sorption isotherms for two enantiomers (E1 and E2) sorbed from individual enantiomer solutions in a hypothetical situation in which E1 was not biodegraded during the sorption experiment, whereas 10% of the initial amount of E2 was lost by biodegradation. The isotherms of the enantiomers were assumed to follow the Freundlich model with C-shape ($K_f = 1$; $1/n_f = 1$), L-shape ($K_f = 1$; $1/n_f = 0.5$), or S-shape ($K_f = 1$; $1/n_f = 2$), coinciding with the sorption

Fig. 3 Hypothetical sorption isotherms (C, L or S-type) separately obtained for two enantiomers (E1 and E2) which followed the Freundlich model where 10% of the initial amount of E2 is biodegraded during the sorption experiment. For E2, sorption points that would result after applying an indirect (solid symbols) or direct (open symbols) methodology to measure the sorbed amounts are shown. The solid line represents the actual Freundlich isotherm for the enantiomers ($C_s = K_f C_e^{1/nf}$). Calculations were performed assuming the following parameters: $K_f = 1$; $1/n_f = 1$ (C-type), 0.5 (L-type) or 2 (S-type); soil to solution ratio of 1:1; range of initial enantiomer concentrations of 0–20 mg/l



points expected for the enantiomer that is not biodegraded during the sorption experiment (E1). The sorbed amounts of E2, however, were assumed to be calculated either indirectly, analyzing the amount of enantiomer remaining in solution, or directly, by extracting the enantiomer actually sorbed. The sorption points for E2 will vary depending on the methodology used to determine the sorbed amount. While the direct methodology will accurately provide the actual amounts of E2 sorbed, following the same isotherm pathway as that of E1, the indirect methodology would lead to overestimating sorption of E2 and misinterpreting sorption as an enantiomer-selective process (E2 > E1). Similar experimental artifacts can arise from inaccuracy in the analytical determination of the enantiomers or because of enantiomer interconversion (enantiomerization) during sorption measurement [22], which should thus be discarded for a correct characterization of sorption enantioselectivity.

Experimental artifacts can also affect desorption experiments. Gámiz et al. [37] observed that biodegradation of R-metalaxyl during desorption from a Mediterranean soil resulted in artificially enhanced hysteresis of this enantiomer in non-sterilized soil. Sorption-desorption hysteresis and its enantioselectivity disappeared after autoclaving the soil to minimize microbial activity. It should be taken into account that the measurement of desorption requires longer shaking times and sample manipulation, which increases the risk of interferences by microbial degradation, even when using pre-sterilized soil samples.

Degradation during the sorption-desorption measurement has traditionally been described as a possible cause of hysteresis [38], but it may become particularly relevant when dealing with natural compounds, which are usually very rapidly biodegraded in soils [39]. Gámiz et al. [34], for example, observed hysteresis in the sorption-desorption of the monoterpene carvone in a pre-autoclaved sandy loam soil, obtaining thermodynamic indexes of irreversibility (TII), as hysteresis descriptors, of 0.38 for R-carvone and 0.65 for S-carvone. These values indicated that hysteresis was enantiomer-selective. An analysis of the sorption-desorption isotherms revealed that the hysteresis for S-carvone was particularly enhanced in the last desorption steps. The authors showed that assuming a total degradation of 10% during desorption was sufficient to explain the observed hysteresis for S-carvone [34].

3 Transformation of Chiral Pesticides in Soils

Enantioselective studies of pesticide degradation routes are important to accurately determine the residues of a particular chiral pesticide, control the contamination problems derived from its use, as well as to determine potential risks of enantiomeric residues to non-target organisms and their final presence in the food chain [17]. As in the case of achiral compounds, the transformation of chiral pesticides in soils can occur through biotic or abiotic pathways [40] and will be affected by factors such as the soil composition and texture, pH, redox conditions, and microbial populations

[24, 34, 41–46]. An additional process that may operate for chiral pesticides is enantiomer interconversion or enantiomerization [47]. Variations in enantiomer fractions should particularly be considered in the transformation of chiral pesticides in soils.

3.1 Abiotic Degradation of Chiral Pesticides

The abiotic transformation of chiral pesticides in soils mainly includes photolysis, hydrolysis, and oxidation/reduction reactions. Generally, abiotic reactions are not enantioselective, and consequently, no significant differences in the enantiomers degradation rate are detected [48]. Nevertheless, discerning the relative importance of abiotic against biotic dissipation processes can be difficult. For instance, the main degradation pathway described for metalaxyl in soils has been reported to be its microbial/enzymatic transformation, implying enantioselectivity in the process [24, 27, 42, 49]. However, Liang et al. [50] showed that, although biotransformation was indeed the predominant pathway for the elimination of R-metalaxyl in soil, both abiotic and biotransformation contribute to the degradation of S-metalaxyl. In the same line, the dissipation of the herbicide imazamox in soil involved both biodegradation and photodegradation [51], and the degradation of zoxamide occurred through hydrolysis and biodegradation [52]. Several mechanisms can thus simultaneously operate in the transformation of chiral pesticides in soils, which may hinder the identification of reactions specifically responsible for enantioselectivity.

3.2 Biotransformation of Chiral Pesticides

The biotransformation of chiral pesticides in the soil arises from the action of enzymes or biological receptors from different microorganisms [10]. The active centers of these macromolecules are usually chiral, whereby, despite the chemical similarity of the enantiomers of a chiral pesticide, the strength of the active center-enantiomer association is usually different. This is the main reason why the biotransformation of chiral pesticides can be enantioselective and why the enantiomers may have different bioactivity and toxicity on target and non-target organisms. Enantioselective biotransformation processes, which play a major role in determining the chiral signatures or enantiomeric fractions of chiral pesticides in the environment [14, 53, 54], can be produced by the following ways described by Müller and Kohler [55]:

1. Two enantioselective enzymes, each one transforming only one enantiomer.
2. Both enantiomers are transformed by the same enzyme at different rates.

3. One enzyme transforms sequentially both enantiomers, i.e., the enzyme initially converts one enantiomer and eventually the other, but only when the former has been completely transformed.
4. Transformation of one enantiomer by one enzyme and isomerization of the other by an isomerase.

3.2.1 Factors Affecting the Biotransformation of Chiral Pesticides in Soils

Data on the factors influencing enantioselective dissipation processes are essential to optimize the bioefficacy of chiral pesticides while preserving environmental safety. In general, soil parameters that influence the enantioselective transformation of chiral pesticides in soils are not fully understood [42, 53], as the biotransformation of chiral pesticides in soils is not always necessarily enantioselective. For example, the herbicide imazaquin, under alkaline and aerobic conditions, did not display changes in the enantiomer fraction during its dissipation in two Mediterranean soils [31]. Analogously, little enantioselectivity was observed in the degradation of the fungicide tebuconazole in soil, with enantiomeric fractions ranging between 0.452 and 0.475 after 180 days of incubation in seven soils under aerobic conditions [56]. Also for tebuconazole, Wang et al. [57] obtained EF values ranging from 0.474 to 0.481 in three soils with different characteristics. Likewise, in an investigation of the dissipation of the fungicide benalaxyl in six different soils, R-benalaxyl dissipated faster than S-benalaxyl in three of the studied soils, whereas the transformation of the fungicide was non-enantioselective for the rest of the soils [29]. In the same work, furalaxyl transformation was also assessed, and similar results were obtained. Different microorganisms present in the soils, together with different physicochemical characteristics and sorption behavior, were identified as the key factors modifying the enantioselectivity of the process [29]. The biotransformation of the chiral insecticide fluxametamide in soil under field conditions was also non-enantioselective [58]. These results are in contrast with other data found in the literature where the biotransformation of chiral pesticides in soils was markedly enantioselective [24, 42, 43, 46, 59, 60]. Differences in the enantioselective biotransformation of chiral pesticides in different soils may depend on the different microbial communities or enzyme levels according to soil properties and locations, variables which should be addressed to characterize the final fate of chiral pesticides in soil [24, 61]. Several important factors that can affect the biotransformation of chiral pesticides in the soil are discussed below (Fig. 4).

Sorption Although sorption is commonly considered a non-enantioselective process, it has been demonstrated that it can indirectly affect the enantioselective biotransformation of chiral pesticides through its influence on their availability to soil microbial degraders. As indicated above, sorption is the main factor controlling the bioavailability and the bioaccessibility of pesticides [62–64]. This became apparent when the environmental behavior of metalaxyl was evaluated in three

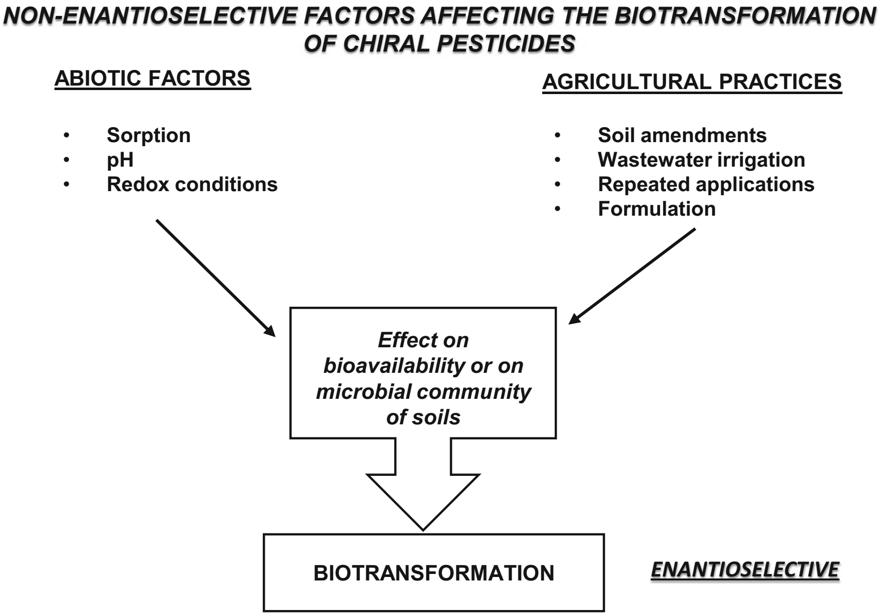


Fig. 4 Factors affecting the biotransformation of chiral pesticides in soils

slightly alkaline soils [24]. R-metalaxyl was preferentially degraded compared to S-metalaxyl in all soils, but the extent of the enantioselective biotransformation of metalaxyl was soil dependent, with the fraction of S-enantiomer in coarse-textured soils achieving greater values than those in fine-clayed soil. The greater sorption observed for metalaxyl in the soil with high clay content reduced the availability of both enantiomers, restraining their biotransformation compared to the coarse texture soils. The authors endorsed the protection of the chiral pesticide to sorption and entrapment in small-size pores, which resulted in longer persistence and more racemic metalaxyl residues in soil [24]. The indirect effect of sorption on the enantioselective biotransformation of chiral pesticides was also observed for the degradation of racemic abscisic acid in soils. Greater persistence and less variation in the enantiomeric fraction were detected in the soil with greater affinity for this acid [32]. Apart from sorption, the participation of soil-specific microorganisms in the biodegradation process could have also contributed to these results [32].

pH The pH has been demonstrated to modify the biotransformation of chiral pesticides in soils [42]. For example, the biotransformation of the herbicide beflubutamid was only slightly enantioselective in alkaline soil, with slower degradation of the bioactive-enantiomer, while the process was more enantioselective in acidic soil [65]. Remarkably, the metabolite of beflubutamid, phenoxybutamide, was also enantioselectively biodegraded in both soils, and interconversion between the enantiomers of the metabolite was observed [65]. Soil pH also altered the enantiomeric fraction of imazethapyr during its transformation under aerobic conditions [66]. In all soils tested, R-imazethapyr degraded faster than S-imazethapyr, with the extent in enantioselectivity (i.e., EF of imazethapyr residues) being soil pH-dependent. The authors attributed this observation to the low sorption and high bioavailability of imazethapyr at greater pH of the soils [66]. Variable behavior was observed for the herbicide imazamox during incubation experiments using soils with different pH, ranging from acidic to neutral. For soils with pH >6.5, the (+)-enantiomer was degraded faster than the (−)-enantiomer, whereas differences between enantiomers were not appreciable in slightly acidic soils. Furthermore, a change in the preferential degradation of the enantiomers occurred in strongly acidic soils [61]. Since biphasic degradation of imazamox enantiomers was detected in all cases, the changes in the transformation of imazamox in soils appeared to be microbial-mediated and dependent on the bioavailability of the herbicide, which has been described to decrease due to nonlinear and time-dependent sorption [61]. Further evidence that the effect of pH on the soil microbial population can modify the enantioselectivity of chiral compounds was observed in the dissipation of the natural compound carvone [34]. The biotransformation of the racemic mixture of carvone in slightly alkaline soil (pH 7.3) occurred very fast, with the S-enantiomer being degraded more rapidly than the R-enantiomer. By acidifying the same soil with HCl to a pH of 5.5, the dissipation of carvone became slower and scarcely enantioselective, with EF values of carvone residues close to 0.5 [34]. Given that the extent of sorption was similar in the pristine and acid-treated soil, the striking behavior was attributed to alterations in the soil microbial activity produced by the change in soil pH [34].

Redox Conditions Redox conditions represent an important parameter influencing the dissipation of chiral pesticides. In an incubation experiment using soil samples taken from 3 to 6 m soil-depth, the preferential degradation of the R-enantiomer of the phenoxyacetic acid herbicide mecoprop (MCPP) was observed under aerobic conditions and at environmentally relevant herbicide concentrations, whereas under anaerobic environments and higher MCPP concentration (mM) the prevalence in the degradation of S-MCPP was observed [67]. The authors found the existence of three types of microbial communities acting primarily depending on environmental conditions [67]. In another study, S-zoxamide was degraded faster than R-zoxamide under aerobic conditions, leading to an enrichment of the bioactive (R) enantiomer in the three types of soils studied, whereas, in an anoxic environment, differences in the degradation rates of S- and R-zoxamide were negligible. Aerobic microorganisms thus appeared to have dictated the biotransformation of zoxamide in an enantioselective manner in contrast to anaerobic microorganisms [52].

Agricultural Practices Agricultural practices and different application regimes of chiral pesticides can influence the availability of the enantiomers and also the nature and activity of the soil microbial population [28, 30, 37, 43, 68]. Furthermore, with the progress of modern agriculture, many novel additives, such as nanoparticles or nanoengineered materials, can reach the soil with consequences on the transformation and transport of chiral pesticides difficult to predict [35, 50].

One of the most extended agricultural practices is the application of organic amendments to improve the fertility of soils by increasing their organic matter and nutrient content. Organic amendments can trigger changes in the microbial activity

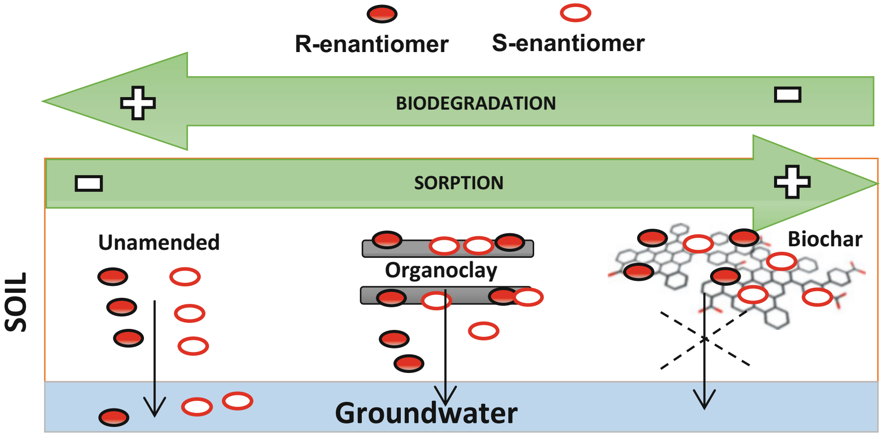


Fig. 5 Conceptual model of the effect of the addition of organic and nanoengineered sorbents to soil on the fate of chiral pesticides

of soils and, as a side effect, the sorption capacity of soils towards pesticides can be also modified [69–73]. Consequently, the enantioselectivity of the biotransformation of chiral pesticides can be influenced by changes in the microbial population, the bioavailability of the pesticide, or both (Fig. 5).

Soil incubation of racemic metalaxyl in unamended soil and in soil amended with olive-mill waste (OMW) resulted in different transformation patterns for the R- and S-metalaxyl enantiomers [28]. In unamended soil, the biotransformation of metalaxyl was highly enantioselective, with the biologically active enantiomer, R-metalaxyl, being preferentially degraded in comparison with S-metalaxyl. At the end of the experiment, the fraction of S-metalaxyl residues reached a value of 0.85. In OMW-amended soil, however, the biotransformation of metalaxyl showed little enantioselectivity and the fraction of S-enantiomer reached the value of 0.53. The organic waste increased the persistence of (active) R-metalaxyl and decreased the persistence of (non-active) S-metalaxyl [28]. Because OMW did not change the sorption capacity of the soil towards metalaxyl enantiomers, the effect of OMW was assigned to a change in the soil microbial population or in the activity of specific microbial degraders, as it had been previously suggested for the transformation of the chiral pesticide mecoprop in peat amended soil [74].

Recently, there has been a growing interest in the evaluation of nanoengineered materials, such as biochar, as amendments and mitigating tool to reduce the environmental impact of pesticides [75], but only a few works have addressed their effects on the enantioselective behavior of chiral pesticides when applied to soils [27, 30, 31, 37, 76]. Gámiz et al. [37] compared the enantioselective behavior of racemic metalaxyl in unamended soil and soil amended with composted olive-mill waste (OMWc) and its biochar. The biotransformation of metalaxyl was less enantioselective in biochar-amended soil, followed by OMWc-amended soil and unamended soil. This was attributed to an increase in the persistence of both metalaxyl enantiomers after the addition of biochar to the soil, caused by greater sorption and higher resistance of metalaxyl enantiomers to be desorbed, which maintained metalaxyl residues more racemic in the presence of biochar. The effect was in agreement with previous works describing the indirect effect of sorption on the availability of chiral pesticides in soils, although changes in the soil microbial activity could not be ruled out. The same trend was observed by López-Cabeza et al. [27], who compared the dissipation of racemic metalaxyl in soils amended with fresh olive-mill waste, composted olive-mill waste, and nanostructured elaidate-modified layered double hydroxide. They found that the amended soils with elaidate-modified layered double hydroxide displayed greater sorption of metalaxyl as compared to the rest of the amendments, which reduced the bioavailability of the enantiomers and maintained metalaxyl residues more racemic in the soils. A lower dissipation rate of metalaxyl enantiomers after the addition of woodchip biochar to a Chinese soil was also observed by You et al. [76]. In this work, although the preferential dissipation of the S-enantiomer as compared to the R-enantiomer occurred, the transformation was less enantioselective due to the indirect effect of metalaxyl sorption in biochar-amended soil. Interestingly, the reduction in the bioavailability of metalaxyl enantiomers led to a greater concentration of fungicide enantiomers in soil but triggered lower concentrations of R and S in the roots as compared to unamended soil. The authors also obtained calculated EF <0.5 indicating preferential accumulation of R-metalaxyl in the lettuce roots [76].

The addition of nanoengineered materials has also been proposed to increase the persistence of enantiomers of natural compounds with the potential to be used as biopesticides, such as abscisic acid (ABA) and carvone [33, 35]. The dissipation of both compounds was assessed in unamended soil and in soil amended with biochar and organically-modified bentonites. The dissipation of ABA mainly elapsed via biodegradation. Besides, the naturally occurring enantiomer S-ABA was always degraded faster than R-ABA (non-natural) in all treatments, and the enantioselectivity of ABA degradation was more pronounced in unamended soil compared to amended soils [33]. Sorption was determined in this work during the incubation experiment and a loss of sorption capacity of the organoclay-amended soil was observed in contrast to progressive sorption in biochar-amended soil, leading to more racemic residues in this latter case. Two different sorption mechanisms were described which explain this different behavior, i.e., surface sorption mechanisms for organoclays and slow (potentially pore filling) kinetics in biochar-amended soil [33]. A similar trend was observed for the dissipation of the monoterpene carvone in unamended soil and soil amended with organoclay and biochar [35]. Although S-carvone was preferentially degraded in all treatments, the greater sorption promoted by the addition of the amendments caused an increase in the half-lives of both enantiomers. The effect was more pronounced for biochar-amended soil, and the authors indicated that the bioavailability of carvone was dictated not only by the extent of sorption but also by the facility of the enantiomers to be desorbed, which was more limited in biochar-amended soil [35].

The addition of nanoparticles, such as TiO_2 or SiO_2, has also been shown to impact the behavior of racemic metalaxyl in soils by their influence on the chemical transformation or the bacterial community of soils [50, 77]. TiO_2 and SiO_2 promoted the chemical transformation of racemic metalaxyl in sterilized soils by the formation of reactive oxygen species (ROS) without changes in the preferential degradation of one enantiomer over the other [50]. DNA analysis demonstrated that the bacterial community was not modified after the addition of the nanoparticles to the soils, indicating that the enhanced transformation of rac-metalaxyl by TiO_2 addition was a chemical transformation [77]. The authors also evaluated the presence of mancozeb in the commercial formulation of metalaxyl and they observed that mancozeb did not induce changes in the enantiomeric fraction of metalaxyl in soil [77]. The addition of ZnO to soil did not affect the transformation of racemic quizalofop-ethyl, in contrast to what was reported for metalaxyl. The authors suggested that the rapid biotransformation of quizalofop-ethyl did not allow the chemical transformation induced by the presence of this photocatalyst [78].

Farming practices such as wastewater irrigation or sewage sludge application can modify the degradation of the chiral fungicide benalaxyl [79]. For example, while wastewater irrigation delayed the transformation of racemic benalaxyl in soil, sewage sludge promoted the degradation of the fungicide, with opposite enantioselectivity between soil and sewage sludge. In the case of sewage sludge, EF values were always >0.5 implying residues enriched in R-benalaxyl, whereas in soil irrigated with wastewater the values were lower than 0.5, representing S-benalaxyl abundance. As observed in the case of olive-mill wastes, this behavior would allow modulating the degradation of more toxic enantiomers, reducing environmental problems associated with their application to soils [79].

Repeated applications of pesticides can induce their accelerated biotransformation due to microbial adaptation [80, 81]. This was observed by Celis et al. [68], who investigated the effect of the repeated application of racemic metalaxyl to soils and found that the biotransformation of R-metalaxyl was enhanced after three successive applications. In contrast, the degradation rate of the non-active S-metalaxyl enantiomer became slower with the repeated applications, which was explained by the occurrence of several mechanisms comprising toxicity of the pesticide or its metabolites to S-metalaxyl degraders, easily degradable soil organic matter depletion with time, and/or time-dependent sorption effects [68].

3.3 Other Aspects to Consider in the Transformation of Chiral Pesticides in Soils

Most of the studies regarding the enantioselective biotransformation of chiral pesticides in soil have been done using racemic mixtures instead of pure enantiomers, due to the limited availability of commercial products. Only a few works have reported the dissipation of purified enantiomers separately in comparison with the racemates. Interestingly, López-Cabeza et al. [31] found that the herbicide imazaquin applied as pure enantiomers to Mediterranean soils was degraded faster than when applied as a racemic mixture of enantiomers. More recently, Gao et al. [82] evaluated the dissipation of the chiral organophosphorus insecticide isofenphos-methyl in soil, either as a racemic mixture or as purified enantiomers, and did not observe differences between them during an incubation experiment performed in three Chinese soils. The enantioselectivity in the biotransformation of this pesticide was suggested to be dependent on the enantiomer itself and its effect on the microbial community of the soils [82]. Therefore, more work is needed to understand possible differences between racemic mixtures and pure enantiomers concerning their degradation in the soil environment.

The recommendation to replace the racemic mixture of a certain pesticide with the corresponding purified active enantiomer requires a deep knowledge of the enantioselectivity of its behavior in the environment. Under certain environmental and even storage conditions, some biologically active enantiomers can be transformed, either biotically or abiotically, into the inactive enantiomer through a process of interconversion between enantiomers or enantiomerization [83]. In these cases, the substitution of the racemic mixture for the active enantiomer would be meaningless, especially under conditions where enantiomerization or racemization occurs rapidly [47]. For instance, the herbicide haloxyfop-methyl, which is rapidly degraded in soils, and its metabolite, haloxyfop acid, underwent enantiomer interconversion in such a manner that S-haloxyfop was converted to R-haloxyfop. The process was biologically mediated since neither degradation nor interconversion took place in sterile soil [84]. Similarly, Buerge et al. [65] did not observe enantiomer interconversion for the chiral pesticide beflubutamid, but did observe the enantiomerization of the main metabolite of this pesticide. This illustrates that assessment of enantiomerization is important not only for the parent compounds but also for their potential transformation products. In this context, in several European countries decreed that only the R-enantiomers of the herbicides dichlorprop and mecoprop will be used, as well as the R (active) enantiomers of all phenoxypropionic acid herbicides, to reduce the amount of herbicide used and avoid possible adverse impacts caused by the S (inactive) enantiomer [1]. It is, therefore, essential to acquire new knowledge when it comes to predicting the behavior of chiral pesticides after their application to agricultural soils, as well as to provide the scientific foundations that allow establishing under which agricultural and environmental conditions it is appropriate to replace racemic pesticide mixtures with the corresponding purified active isomers.

Few studies have been devoted to assessing the behavior of chiral pesticides under field conditions [85]. These can alter the degradation pattern of chiral pesticides affecting their degradation and eventually the enantioselectivity. In the field, several attenuation processes including leaching, runoff, volatilization, or chemical transformations can simultaneously operate [64]. This has been observed for the herbicide imazamox, which was found to be enantioselectively degraded via microbial attack when the dissipation experiment was performed under dark, controlled conditions in the laboratory [51], whereas non-enantioselective photolysis was identified as the predominant degradation pathway when degradation was appraised under natural sunlight exposure [51]. Several authors have studied the dissipation of tebuconazole in soils under real conditions and little enantioselectivity was observed for Chinese [86] and Mediterranean [30] soils. It was pointed out that the high half-lives of tebuconazole in soils probably hindered the development of enantioselectivity within the time-scale of the experiment [30]. Conversely, in the same field study, the enantioselective behavior of the fungicide metalaxyl was comparable to that observed in the laboratory, with R-metalaxyl being degraded more rapidly than S-metalaxyl in an alkaline soil under field conditions [30]. The addition of clay and biochar impacted the enantioselectivity of metalaxyl dissipation, with metalaxyl residues remaining more racemic in the amended soil due to the effect of sorption, as proposed previously in laboratory incubation studies [27, 37]. Li et al. [58] evaluated the degradation of the novel insecticide fluxametamide under field conditions and concluded that the process was non-enantioselective, whereby the application of the purified active S-enantiomer was encouraged to reduce the environmental impact and toxicity of this pesticide [58]. More studies to discern whether enantioselective data observed at laboratory scale are reproduced under real field conditions are particularly needed.

4 Leaching of Chiral Pesticides in Soils

The leaching of chiral pesticide enantiomers will be intimately related to their sorption-desorption and degradation in the soil. Consequently, if changes in the enantiomeric fraction occur during these processes, pesticide residues in leachates will reflect such changes (Fig. 6). Celis et al. [24] described several hypothetical leaching patterns which can be observed after the application of a racemic mixture of two chiral pesticide enantiomers to a soil column (Fig. 6).

If the enantiomers are equally sorbed and transformed during leaching, the elution curves of both enantiomers should overlap (Fig. 6a). This has been observed for the herbicide imazaquin; its rapid leaching and long persistence in soil did not generate significant variations in the EF values of the herbicide residues detected in leachates during a column experiment [31]. However, the most typical situation is depicted in Fig. 6b, where the enantiomers are sorbed to the same extent but one of them is degraded faster than the other during the vertical transport. This behavior has been observed after the application of racemic mixtures of metalaxyl, benalaxyl, and furalaxyl to soil columns [24, 29]. In these cases, the magnitude of the enantioselectivity in leaching will depend on the difference between the degradation rates of the enantiomers. EF values will be further from 0.5 with increasing enantioselectivity of the biotransformation process, which, in turn, may be affected by the sorption extent. Celis et al. [24], for example, observed noticeable enantioselectivity in the leaching of racemic metalaxyl in columns packed with a soil in which the fungicide displayed low sorption and strong enantioselective biotransformation. It should be noted, however, that divergences in degradation under incubation and column leaching conditions can occur. For instance, Gámiz et al. [32] detected greater amounts of the enantiomers of abscisic acid in column leachates from a soil where none of the enantiomers displayed a particularly long

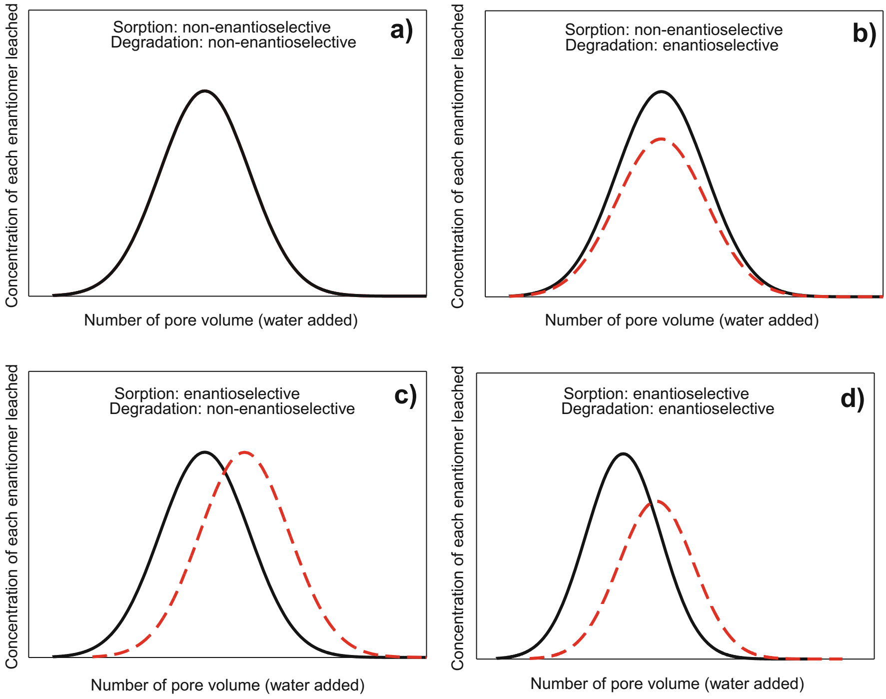


Fig. 6 Schematic representation of theoretical breakthrough curves for a racemic mixture of a chiral pesticide (black and red lines represent the two enantiomers) in soil columns where: (**a**) the two enantiomers are equally sorbed and degraded (**b**) the two enantiomers are equally sorbed but enantiomer 2 (red line) is degraded to a greater extent than enantiomer 1 (black line) during leaching, (**c**) the two enantiomers are equally degraded but enantiomer 2 (red line) is sorbed to a greater extent than enantiomer 1 (black line), and (**d**) enantiomer 2 (red line) is sorbed and degraded to a greater extent than enantiomer 1 (black line). The area below each curve represents the total amount of enantiomer leached. Adapted from Celis et al. [24]

persistence under incubation conditions. The authors attributed this behavior to a degradation lag phase during which abscisic acid rapidly leached through the soil column and the different experimental conditions in the incubation and column experiments (static and aerobic in the incubation tests versus dynamic and partially anaerobic in the column tests). It is known that the redox environment can affect the enantioselective biotransformation of chiral pesticides due to its impact on degrading microorganisms [42, 87], and the soil microbial community is expected to be affected by oxygen availability in saturated soil columns [32].

The leaching of non-racemic mixtures of chiral pesticide enantiomers has been little explored. Gámiz et al. [22] observed a change in the enantiomer fraction of a solution enriched in the R-enantiomer of metalaxyl during leaching through a soil column, even though the degradation of the enantiomers along the experiment was negligible. This behavior was attributed to the preferential sorption of the more abundant (R) enantiomer, as previously discussed in Sect. 2 [21]. The fact that, for both enantiomers, the total amount leached was >95% demonstrated that little degradation or enantiomer interconversion occurred during leaching. This case, which corresponds to that shown in Fig. 6c, provided direct evidence of how the enantioselective sorption of a chiral pesticide in soil, if it occurred, would affect the availability of its enantiomers to undergo other environmental processes.

The addition of organic amendments to soils can have an important impact on the leaching of chiral pesticide enantiomers, either by directly affecting their biodegradation patterns or by the indirect effect exerted by the sorption of the enantiomers on the amendments. Sorption can protect the enantiomers from biological degradation, but may also increase their residence time within the soil column, enhancing the chance of microbial degradation. Gámiz et al. [28] observed that the leaching of metalaxyl was less enantioselective in olive-mill waste-amended soil than in unamended soil. As the organic amendment had a negligible effect on the sorption of metalaxyl enantiomers, less enantioselective biodegradation of metalaxyl in the amended soil resulted in metalaxyl residues in leachates being more racemic compared to the unamended soil. In a subsequent study, the authors compared the leaching of a racemic mixture of R- and S-metalaxyl in soil columns amended with composted olive-mill waste and its biochar [37]. The mobility of both enantiomers was almost suppressed after amending the soil with biochar, whereas considerable amounts of R- and S-metalaxyl leached from unamended soil and from the composted olive-mill waste-amended soil. It was remarkable that while the fraction of S-enantiomer in leachates for the three treatments was similar (EF = 0.85–0.89), metalaxyl residues remaining in the biochar-amended soil columns had enantiomer fractions closer to 0.5 (EF = 0.70). It was concluded that the enhanced sorption in the biochar-amended soil columns protected metalaxyl from enantioselective biotransformation, maintaining metalaxyl residues within the soil column more racemic than those collected in the column leachates. Results of López-Cabeza et al. [31] did not reveal enantiomer-selective leaching of the herbicide imazaquin in two agricultural soils amended with composted olive-mill waste, organoclay, or biochar. Although some treatments impacted the sorption of the imazaquin enantiomers, a small incidence of biodegradation processes made the effect of the amendments on leaching enantioselectivity negligible [31].

It is worthy to note that the availability of the enantiomers of a chiral pesticide will depend not only on sorption but also on its desorption. The use of nanoengineered materials has been proposed to control the degradation and transport losses of natural compounds in soil, which can highly reduce their activity as biopesticides. Very promising results were obtained for the chiral compounds abscisic acid and carvone, for which organoclays and biochars increased sorption and delayed dissipation, allowing the enantiomers to remain longer in the soil [33, 35]. For both compounds, the influence of sorption was more noticeable for biochar-amended soil than for organoclay-amended soil. The amounts of abscisic acid and carvone leached from biochar-amended soils were lower than those from unamended or organoclay-amended soil, and abscisic acid and carvone residues remaining in the soil at the end of the experiment were more racemic. Weaker sorption and easier desorption of the enantiomers in unamended soil and organoclays-amended soil, in contrast to high resistance to desorption from biochar-amended soil, could explain these results [33, 35]. For these reasons, it is expected that biochar could protect these compounds from biotransformation and transport losses and increase their persistence in soils.

5 Effect of Chiral Pesticides on the Microbial Community of Soils

All factors that may influence, in one way or another, the soil microbial population or its activity have the potential to impact the enantioselectivity of the biotransformation of chiral pesticides in soils (Fig. 4). Current intensive agricultural practices alter the biodiversity of soils and their microbial populations [88], which claims for a better understanding of the effect of chiral pesticides on the soil microbial community and vice versa. To date, this aspect has been largely overlooked, probably due to the complexity of interactions between chiral compounds and soil microorganisms. The underlying mechanisms of these interactions, together with the relationships between the soil microbial diversity and the biotransformation of chiral pesticides, remain largely unknown [89]. Zhang et al. [90] observed that R- to S-enantiomer interconversion of the chiral phenylpyrazole insecticide ethiprole in soil proliferated within the groups *Luteimonas*, *Comamonadaceae*, and *Xanthomonadaceae* in bacteria. Zhou et al. [89] found that enantioselectivity in the biotransformation of racemic quizalofop-ethyl was correlated with bacterial structure, while the transformation rate was mainly dictated by the bacterial richness and abundance. At higher soil microbial diversity, the enantioselective transformation of quizalofop-ethyl became more complex and difficult to predict [89]. More recently, Liu et al. [91] demonstrated that imazethapyr enantiomers changed the *Arabidopsis thaliana* rhizosphere microorganism composition and root exudates, with only R-imazethapyr encompassing an inhibitory effect on plant biomass, but not S-imazethapyr. Furthermore, soil treatment with R-imazethapyr resulted in a greater increase in the relative abundance of beneficial rhizosphere microbes, such as *Bacillus* and *Ramlibacter*, compared to S-enantiomer treatment. This indicated the possible accumulation of some microorganisms in the rhizosphere in order to reduce herbicide stress [91]. In another work, the application of the novel acaricide cyflumetofen to soil altered the soil microbial population by reducing the bacterial abundance [92]. Such alteration was enantiomer-selective. The cyflumetofen enantiomers also had an impact on the abundance of N_2-fixing bacteria, in such a way that (+)-cyflumetofen could promote nitrification whereas (−)-cyflumetofen reduced the abundance of *amoA* gene, that is, negatively affected the nitrification in the nitrogen cycle [92]. These results encourage further research on the effects of pesticide chirality on soil microbial communities, which will influence the function and structure of the agricultural ecosystem. This information is essential for a better characterization of the global behavior and potential alterations caused by the presence of chiral pesticides in soils [90].

6 Effect of Chiral Pesticides on Target and Non-target Organisms

The final bioactivity and toxicity of chiral pesticides will be subjected to the transfer and transformation processes that they may undergo in soils. Both bioactivity and toxicity are commonly enantioselective since the molecular target of these pesticides is usually an enzyme or a biological receptor whose active center is also chiral, so it preferentially reacts with one of the enantiomers [10].

6.1 Enantioselective Bioactivity of Chiral Pesticides Against Target Organisms

In the case of chiral herbicides, some of the most common biochemical targets or modes of action that are inhibited by them are acetyl-coenzyme A carboxylase, an essential enzyme in long-chain fatty acid biosynthesis [93]; cellulose biosynthesis, acetohydroxy acid synthase/acetolactase synthase [94] and 4-hydroxy-phenylpyrovate dioxygenase [2]. Determining the structure of complexes formed between the enzymes and the herbicide enantiomer has been possible due to the availability of molecular docking computer tools (Autodock) [95]. For instance, imidazolinones are a group of chiral herbicides targeting acetohydroxyacid synthase, which is a key enzyme in the branched-chain amino acid biosynthesis pathway. By molecular docking, several studies demonstrated that the conformation of the R-enantiomer exhibited better binding modes than the S-enantiomer to the enzyme, which led to a greater inhibition [94, 96].

The bioactivity of fungicides against a large number of pathogens is also enantioselective. The main targets of fungicides are usually the respiratory chain, addressing the biochemical target succinate dehydrogenase [97] and cytochrome bc1; the cellulose biosynthesis by targeting the cellulose synthase 3 (CesA3) enzyme; the oxysterol-binding protein [98]; and the ergosterol biosynthesis, an essential component of the fungi's membrane, by targeting the CYP51B enzyme [2]. The latter is the mode of action of the triazole fungicides, a large and widely used group of fungicides of which approximately 84% are chiral [99]. The bioactivity of R-enantiomer of triazole fungicide is usually greater than that of S-enantiomer. In several works, the interaction between triazole fungicides and the CYP51B enzyme was studied and it was concluded that the R-enantiomers had better binding modes than S-enantiomers to the enzyme, which resulted in a more effective inhibition of the biosynthesis of ergosterol [99, 100].

The chiral insecticides also have enantioselective bioactivity due to different interaction between the enantiomers and the action site of the enzymes. An example is fluxametamide, whose stronger affinity of its S-enantiomer for the γ-aminobutyric acid receptor led to higher bioactivity [58].

6.2 Enantioselective Toxicity of Chiral Pesticides to Non-target Organisms

In most cases, the enantiomer active against the target weed is also the one that is most toxic to non-target plants since the objective enzyme is usually the same. Thus, for imidazolinone herbicides, the active R-enantiomer is more toxic than the inactive S-enantiomers both against target-active weeds (*Echinochloa crus-galli* or *A. thaliana*) and against non-target species such as *Oryza sativa* (rice) [101] and *Zea mays* L. (maize) [102]. Although the study of toxicology of herbicides is mainly focused on plants, these agrochemicals may be transported by runoff to water bodies and affect other organisms as cyanobacteria or microalgae. In the case of algae, the enantioselective effect of a chiral pesticide is usually opposite than vesicular plants [95]. Thus, the toxic effect of R-enantiomer of several chiral herbicides (including napropamide, acetochlor, propisochlor, and diclofop) on freshwater cyanobacteria and algae was less than that of the S-enantiomer [103, 104]. This inverse toxicity of the enantiomers suggested that the interaction pattern could differ greatly in different biological systems [104]. In this specific case, since the toxicity is mainly due to the S-enantiomer, the exclusive application of the active R-enantiomer may be less harmful than the application of the racemic mixture.

As a basis for the risk assessment, the enantioselectivity of toxicity to non-target organisms of chiral fungicides and insecticides must be evaluated in different terrestrial (nematodes, insects, and reptiles among others) and aquatic model organisms that cover different trophic levels (generally algae and crustaceans, fishes).

In toxicity assessments of chiral pesticides, the toxicity of the racemate is roughly intermediate between the toxicity of each enantiomer separately. However, on occasion, it has been observed that the toxicity of the racemic mixture is greater than or equal to that of the individual enantiomers, which would be indicative of a strong synergy between the toxic effect of the enantiomers against these species [56, 100, 105]. Thus, the effect of racemic mixtures on organisms cannot be predicted from the effect of the enantiomers and must be studied separately [56]. In these cases, the application of the active enantiomer instead of the racemate would maintain the activity and minimize risk on non-target organisms.

7 Future Perspectives

Future research in the field of chiral pesticides should be aimed at setting up the scientific foundations to establish under which agricultural and environmental conditions it would be appropriate to replace chiral pesticide racemic mixtures with the corresponding purified active enantiomer. This information can be valuable to the companies in the sector interested in the production of crop protection products at a large scale. Furthermore, information on the enantioselective environmental processes could influence policies and guidelines on management, conservation, and restoration of soils. For this purpose, the following issues are demanded:

- Better understanding of the effect of chiral pesticides and different agricultural practices on the soil microbial community and vice versa.
- To establish the interconnection of abiotic and biotic factors in the degradation of pesticides together with studies using pure enantiomers to assess the relevance of enantiomerization mechanisms. This is important not only for the parent compounds but also for their potential transformation products.
- To contrast the results obtained in laboratory-scale experiments with experiments regarding the environmental fate of chiral pesticides at field-scale studies, as the latter are very scarce.

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

Maria C. Vagi and Andreas S. Petsas

Contents

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^{-1} (dry weight, dw), 7.94–636 ng L^{-1}, and 0.017–31.3 ng g^{-1} (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 μg 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, nematicides, 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].

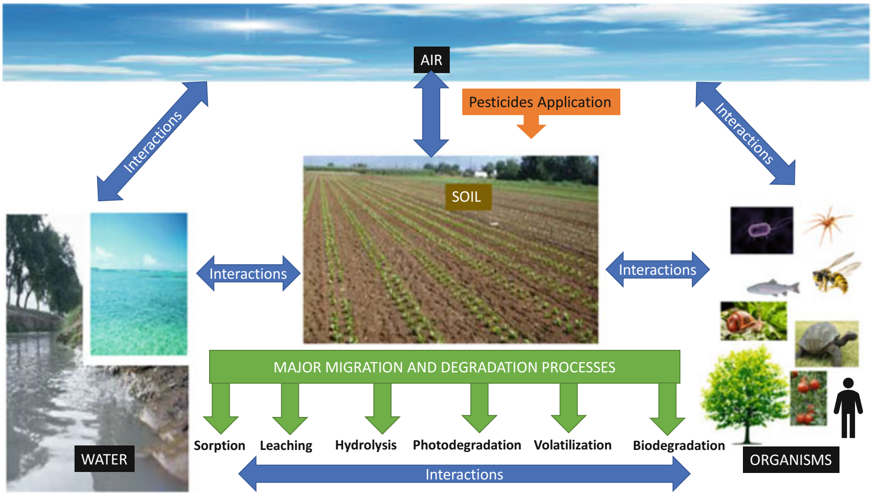

Fig. 1 Major migration and degradation processes to which pesticides substances are subjected to after their application in the field and interactions between other environmental compartments

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.

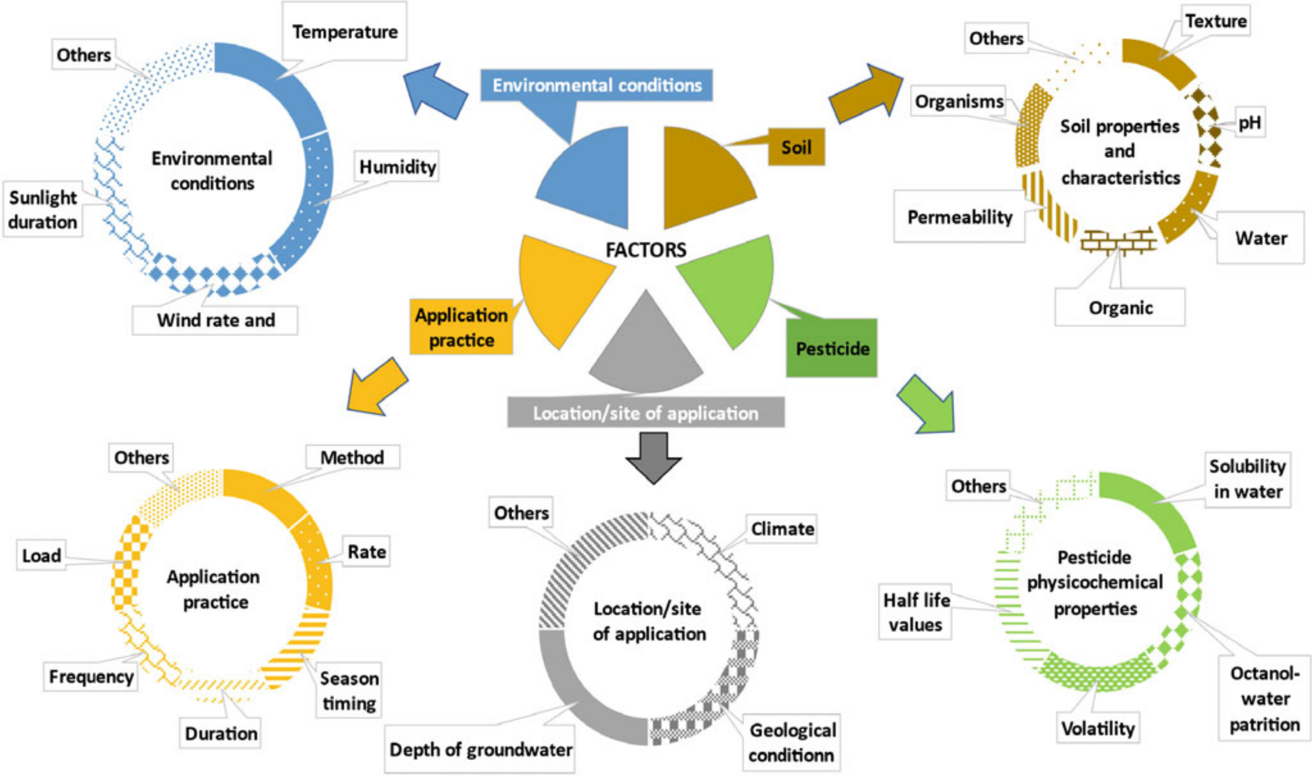

Fig. 2 Principal factors that affect the environmental fate of pesticides [Adapted from Pietrzak et al. [10], after Perez-Lucas et al. [11] and modified]

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:

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

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

$$q_e = \frac{K_L * b * C_e}{1 + b * C_e} \tag{2}$$

$$\frac{C_e}{q_e} = \frac{1}{K_L * q_m} + \frac{C_e}{q_m} \tag{3}$$

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:

$$\frac{q_e}{q_m} = b_e * C_e^{-\frac{q_e}{q_m}} \tag{4}$$

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

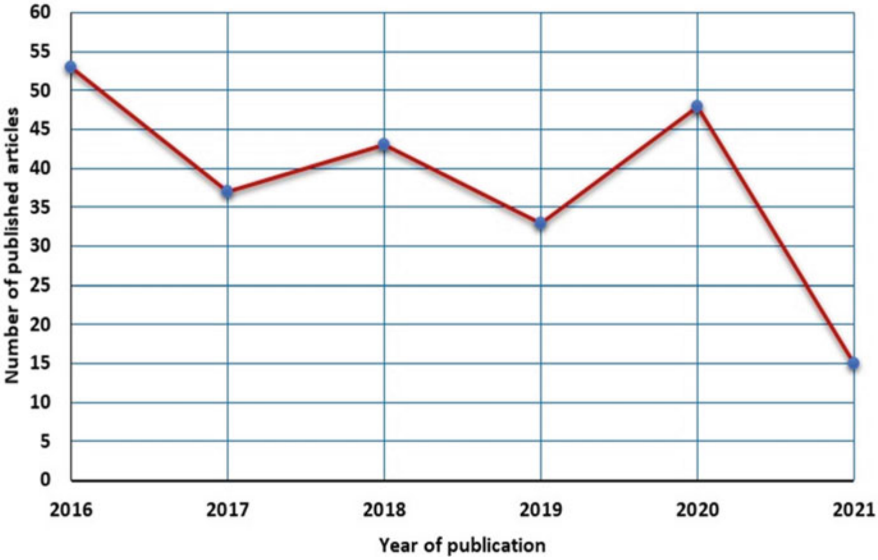

Fig. 3 Annual number of records published during the period from 01/01/2016 to 30/06/2021 regarding the (ad)sorption, desorption, and leaching processes of pesticides into soil/water systems. The plotted data have been located by "Scopus Database" by entering the keywords "pesticide," and "soil," and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

the longer half-lives that can remain in soil at levels above several hundreds of μg 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), sulfonylurea 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]
			Dissipation	[36]
2	Acetamiprid	Neonicotinoid insecticides	(Ad)sorption/ desorption	[37–39]
			Vertical mobility	[39]
3	Acetochlor	Anilide herbicides (Chloroacetanilides)	(Ad)sorption/ desorption	[40]
4	Alachlor	Anilide herbicides (Chloroacetanilides)	(Ad)sorption/ desorption	[41–45]
			Leaching	[41, 45]
5	Ametryn	Triazine herbicides (Thiotriazines)	Vertical transport	[24]
			Leaching	[46]
6	Aminocyclopyrachlor	Pyrimidine, cyclopropane and organochlorine pesticides	(Ad)sorption/ desorption	[47, 48]
			Leaching	[47, 48]
7	*AMPA* (Aminomethylphosphonic acid)	Aminomethylphosphonic acids	Vertical mobility	[1]
8	Atrazine (and transformation product: 2-hydroxyatrazine)	Triazine herbicides	(Ad)sorption/ desorption	[34, 35, 49–66]
			Leaching	[46, 53, 66–68]
			Runoff in soil	[53]
			Vertical mobility	[24]
			Dissipation	[58]
9	Azimsulfuron	Sulfonylurea herbicides (*N*-sulfonylureas)	(Ad)sorption/ desorption	[69]

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

(continued)

Table 1 (continued)

No.	Pesticide name	Chemical group	Process studied	Reference(s)
			Adsorption/desorption	[87]
21	Cadusafos	Organophosphorus insecticides	Adsorption/desorption	[71, 88]
			Dissipation	[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	Crotoxyphos	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	[138, 145, 146]
			Dissipation	[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	[20, 84, 103, 147–159]
			Leaching	[67, 117, 159–161]
			Dissipation	[145]
			Vertical mobility	[24, 84]
59	2,4-D (2,4-Dichlorophenoxyacetic acid)	Phenoxy herbicides	Adsorption/desorption	[34, 90, 150, 162–166]
			Dissipation	[85]
			Diffusion	[164]
			Vertical mobility	[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	[121, 123, 168]
			Dissipation	[121]
65	Epoxiconazole	Conazole fungicides	Adsorption/desorption	[58, 169]
			Dissipation	[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 desulfinyl, 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	Sulfonylurea 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 nematicides	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	Metaldehyde	Other pesticides: Molluscacides, Tetraoxacyclooctanes	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 (Chloroacetanilides)	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	Myclobutanil	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	[22, 175, 221]
			Leaching	[82, 175, 221]
131	Pendimethalin	Dinitroaniline herbicides	Adsorption/desorption	[58, 138, 145, 176, 222, 223]
			Dissipation	[58, 145]
132	Penflufen	Organofluorine aromatic amide fungicides, Pyrazole carboximides	Adsorption/desorption	[177]
133	Penoxsulam	Amide herbicides	Adsorption/desorption	[69]
134	Penthachlorophenol	Organochlorines, phenols	Adsorption/desorption	[224–226]
			Leaching	[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	[189]
			Leaching	[68]
142	Pirimicarb	Carbamate insecticides	Adsorption/desorption	[123, 127]
143	Pirimiphos ethyl	Organophosphorus insecticides	Adsorption/desorption	[123]
144	Prochloraz	Amide fungicides (Imidazoles)	Adsorption/desorption	[58, 123]
			Dissipation	[58]
145	Procymidone	Dicarboximide fungicides	Adsorption/desorption	[71, 131, 134]
			Leaching	[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	Quinoxyfen	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	Sulfotep	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	Terbuthylazine	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	Thoazole 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	*N*-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]
			Dissipation	[204]
181	Tribenuron-methyl	Sulfonylurea herbicides	Dissipation	[85]
182	Trichlorfon (or Metrifonate)	Organophosphorus insecticides	Adsorption/desorption	[28]
183	Triclosan	Polychloro phenoxy phenols	Adsorption/desorption	[156]
184	Triclopyr	Pyridine herbicides	Adsorption/desorption	[173]
185	Trifloxystrobin	Strobilurin fungicides	Adsorption/desorption	[71]
186	Triflumezopyrim	Pyridopyrimidinone insecticides	Adsorption/desorption	[247]

Table 2 Classification of **r**eports 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); Chlorothalinil (3); 2-Chlorophenol (1); DDT (2); Dicofol (1), 2,4-Dichlorophenol (1); Endosulfan (3); Pentachlorophenol (4)
10	Organophosphorus insecticides, herbicides, fungicides, and nematicides	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); Toclofos-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); Terbuthylazine (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); Quinoxyfen (1); Sedaxane (1); Sulfentrazone (2); Tetradifon (1); Thiabendazole (1); Thymol (1); Triadimenol (1); Triclosan (1); Triflumezopyrim (1)

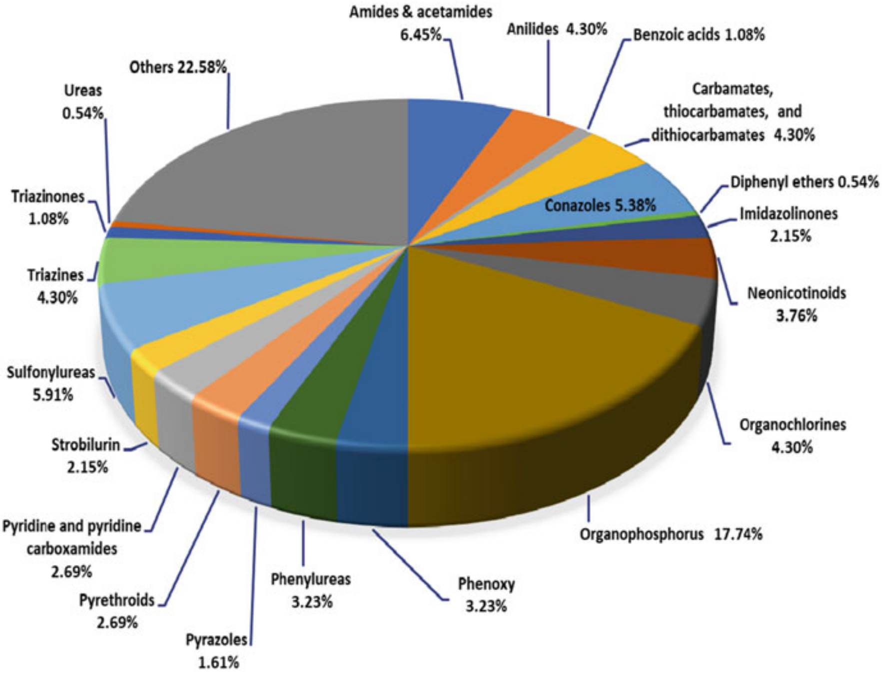

Fig. 4 Overall relative frequency of reports for different chemical groups of pesticides concerning their (ad)sorption/desorption and leaching phenomena in natural soil matrices overviewed in present review. The search was based on “Scopus Database” using as keywords the terms pesticide, soil, and sorption 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 $(\text{mg/kg})(\text{mg/L})^{-n}$) 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^{-1})	% OC	pH	Other information available		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^{-1}): $Al_{pyz} = 5.1^a$; $Fe_{pyz} = 0.62^a$; $Al_{ox} = 13^b$; $Fe_{ox} = 6.7^b$; $Si_{ox} = 1.0^b$; $Al_{DCB} = 1.1^c$; $Fe_{DCB} = 6.9^c$	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^{-1}) = 0.44; $P_2O_5\,(g\,kg^{-1}) = 0.02$; $K_2O\,(g\,kg^{-1}) = 0.043$ Soil microbial biomass carbon (mg C kg^{-1}) = 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)

	Soil content and physicochemical properties								Experimental method/ Isotherm model	Estimated parameters		
Pesticide name (chemical class)	Type (texture)	% Sand	% Silt	% Clay	CEC (cmol kg^{-1})	% OC	pH	Other information available		Sorption process	Desorption process	Reference
Clothianidin (neonicotinoid)	Black soil (loam)	52	42	6	61.3	3.08	7.2 (in $CaCl_2$)	Available nutrients (mg kg^{-1}): $N = 279$, $P = 52.2$; electrical conductivity (dS $m^{-1})^d = 524$	Batch equilibrium/ 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 $CaCl_2$)	Available nutrients (mg kg^{-1}): $N = 158$, $P = 29.6$; electrical conductivity (dS $m^{-1})^d = 80.1$		$K_F = 1.08$ $n_F = 0.991$ $R^2 = 0.996$	$K_F = 1.86$ $n_F = 0.977$ $R^2 = 0.982$	
	Paddy soil (clay loam)	32	46	22	14.2	1.43	4.4 (in $CaCl_2$)	Available nutrients (mg kg^{-1}): $N = 115$, $P = 22.7$; electrical conductivity (dS $m^{-1})^d = 34.1$		$K_F = 2.75$ $n_F = 0.779$ $R^2 = 0.956$	$K_F = 4.04$ $n_F = 0.594$ $R^2 = 0.951$	
	Red soil (clay loam)	48	34	18	11.9	0.110	3.8 (in $CaCl_2$)	Available nutrients (mg kg^{-1}): $N = 33.8$, $P = 2.10$; electrical conductivity (dS $m^{-1})^d = 157$		$K_F = 0.992$ $n_F = 0.998$ $R^2 = 0.975$	$K_F = 1.32$ $n_F = 0.921$ $R^2 = 0.976$	
	Vegetable garden soil (silt loam) Depth fractions: • 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 equilibrium/ 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):	[133]

	• 250–400 mm									$R^2 = 0.99$; $K_{oc} = 775$	$K_d = 0.52$ $R^2 = 0.98$	
	Farm soil (fine sandy loam) Depth fractions: • 0–130 mm • 130–250 mm • 250–400 mm			17.0 31.3 30.3	18.9 (0–130 mm) 19.8 (130–250 mm) 20.8 (250–400 mm)	0.30 0.24 0.21	6.08 (0–130 mm) 6.59 (130–250 mm) 6.38 (250–400 mm)			(0–130 mm): $K_d = 1.45$; $R^2 = 0.99$; $K_{oc} = 483$ (130–250 mm): $K_d = 1.17$; $R^2 = 0.99$; $K_{oc} = 487$ (250–400 mm): $K_d = 1.13$ $R^2 = 0.99$; $K_{oc} = 538$	(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): $K_d = 0.82$ $R^2 = 0.99$	
	Farm soil (fine sandy loam) Depth fractions: • 0–130 mm • 130–250 mm • 250–400 mm			14.5 34.3 38.3	20.3 (0–130 mm) 22.9 (130–250 mm) 19.6 (250–400 mm)	0.64 0.40 0.37	7.72 (0–130 mm) 8.06 (130–250 mm) 7.92 (250–400 mm)			(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	13	10	77		2.03	4.2		Batch equilibrium/ Freundlich	$K_F = 4.30$ $1/n_F = 0.81$ $K_{oc} = 212.06$		[84]
Imidacloprid (neonicotinoid)	Black soil (loam)	52	42	6	61.3	3.08	7.2 (in $CaCl_2$)	Available nutrients (mg kg^{-1}): $N = 279$, $P = 52.2$; electrical	Batch equilibrium/ Freundlich	$K_F = 3.42$ $n_F = 0.862$ $R^2 = 0.997$	$K_F = 3.76$ $n_F = 0.725$ $R^2 = 0.975$	[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 (cmol kg^{-1})	% OC	pH	Other information available		Sorption process	Desorption process	
								conductivity $(dS\ m^{-1})^d = 524$				
	Fluvo-aquic soil (loam)	49	42	9	18.3	1.26	4.9 (in $CaCl_2$)	Available nutrients ($mg\ kg^{-1}$): $N = 158$, $P = 29.6$; electrical conductivity $(dS\ m^{-1})^d = 80.1$		$K_F = 2.36$ $n_F = 0.987$ $R^2 = 0.953$	$K_F = 3.27$ $n_F = 0.919$ $R^2 = 0.953$	
	Paddy soil (clay loam)	32	46	22	14.2	1.43	4.4 (in $CaCl_2$)	Available nutrients ($mg\ kg^{-1}$): $N = 115$, $P = 22.7$; electrical conductivity $(dS\ m^{-1})^d = 34.1$		$K_F = 2.62$ $n_F = 0.805$ $R^2 = 0.969$	$K_F = 3.50$ $n_F = 0.650$ $R^2 = 0.963$	
	Red soil (clay loam)	48	34	18	11.9	0.110	3.8 (in $CaCl_2$)	Available nutrients ($mg\ kg^{-1}$): $N = 33.8$, $P = 2.10$; electrical conductivity $(dS\ m^{-1})^d = 157$		$K_F = 1.01$ $n_F = 1.02$ $R^2 = 0.994$	$K_F = 1.20$ $n_F = 1.02$ $R^2 = 0.927$	
Isoproturon (Phenylurea)	Field soil (Sandy loam)	89.5	6.8	3.7		1.52	7.53 (in $CaCl_2$)	Total $N\ (g\ kg^{-1}) = 0.44$; $P_2O_5\ (g\ kg^{-1}) = 0.02$; $K_2O\ (g\ kg^{-1}) = 0.043$ Soil microbial biomass carbon ($mg\ C\ kg^{-1}$) = 160.2	Batch equilibrium/ Freundlich	Active ingredient: $K_F = 4.00$ $n_F = 0.885$ $R^2 = 0.974$ $K_{foc} = 263.3$ Commercial formulation: $K_F = 4.99$ $n_F = 0.725$ $R^2 = 0.998$ $K_{oc} = 328.3$		[122]

Simazine (Triazine)	Grassland soil (Sandy loam)						5.94 ± 0.15	Water holding capacity (%) = 74.97 Electrical conductivity (μS m^{-1}) = 87.73 Total carbon (%) = 3.10; Total nitrogen (%) = 0.34; DOC (g kg^{-1}) = 15.25	Batch equilibrium/L and Freundlich	$K_L = 0.0037$ $q_m = 15.75$ $R^2 = 0.192$		[233]
										$K_F = 0.005$; $n_F = 0.940$; $R^2 = 0.988$		
Tebuconazole (Triazole)	Field soil (Sandy loam)	89.5	6.8	3.7		1.52	7.53 (in water)	Total N (g kg^{-1}) = 0.44; P_2O_5 (g kg^{-1}) = 0.02; K_2O in (g kg^{-1}) = 0.043 Soil microbial biomass carbon (mg C kg^{-1}) = 160.2	Batch equilibrium/ 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	3.08	7.2 (in $CaCl_2$)	Available nutrients (mg kg^{-1}): $N = 279$, $P = 52.2$; electrical conductivity (dS $m^{-1})^d = 524$	Batch equilibrium/ Freundlich	$K_F = 9.06$ $n_F = 0.806$ $R^2 = 0.998$	$K_F = 10.9$ $n_F = 0.717$ $R^2 = 0.987$	[135]
	Fluvo-aquic soil (loam)	49	42	9	18.3	1.26	4.9 (in $CaCl_2$)	Available nutrients (mg kg^{-1}): $N = 158$, $P = 29.6$; electrical conductivity (dS $m^{-1})^d = 80.1$		$K_F = 3.40$ $n_F = 0.842$ $R^2 = 0.995$	$K_F = 4.28$ $n_F = 0.770$ $R^2 = 0.984$	
	Paddy soil (clay loam)	32	46	22	14.2	1.43	4.4 (in $CaCl_2$)	Available nutrients (mg kg^{-1}): $N = 115$, $P = 22.7$; electrical conductivity (dS $m^{-1})^d = 34.1$		$K_F = 4.70$ $n_F = 0.719$ $R^2 = 0.994$	$K_F = 5.49$ $n_F = 0.645$ $R^2 = 0.955$	

(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 (cmol kg^{-1})	% OC	pH	Other information available		Sorption process	Desorption process	
	Red soil (clay loam)	48	34	18	11.9	0.110	3.8 (in $CaCl_2$)	Available nutrients (mg kg^{-1}): $N = 33.8$, $P = 2.10$; electrical conductivity (dS $m^{-1})^d = 157$		$K_F = 1.16$ $n_F = 0.984$ $R^2 = 0.996$	$K_F = 1.55$ $n_F = 0.943$ $R^2 = 0.989$	
	Agricultural soil	31	58	11	8.1	1.2	8.1	Calcaric fluvisol devoted to different irrigated crops such as corn, tobacco, and fruit trees. $CaCO_3(\%) = 26$ Electrical conductivity (dS $m^{-1})^d = 1.2$	Batch equilibrium and column/ Freundlich and Henry's linear	$K_F = 5.3$; $1/n_F = 0.60$ $R^2 = 0.989$ $K_d = 4.0$ $R^2 = 0.882$ $K_{oc} = 331$		[239]
Thiamethoxam (neonicotinoid)	Vegetable garden soil (silt loam) Depth fractions: • 0–130 mm • 130–250 mm • 250–400 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 equilibrium/ 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 fractions:			17.0 31.3 30.3	18.9 (0–130 mm) 19.8 (130–	0.30 0.24 0.21	6.08 (0–130 mm) 6.59 (130–			(0–130 mm): $K_d = 1.48$; $R^2 = 0.99$; $K_{oc} = 493$ (130–250 mm):	(0–130 mm): $K_d = 0.65$; $R^2 = 0.98$ (130–250 mm):	

	• 0– 130 mm • 130– 250 mm • 250– 400 mm				250 mm) 20.8 (250– 400 mm)		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): $K_d = 0.60$ $R^2 = 0.96$	
	Farm soil (fine sandy loam) Depth fractions: • 0- 130 mm • 130– 250 mm • 250– 400 mm			14.5 34.3 38.3	20.3 (0– 130 mm) 22.9 (130– 250 mm) 19.6 (250– 400 mm)	0.64 0.40 0.37	7.72 (0– 130 mm) 8.06 (130– 250 mm) 7.92 (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

[a] Pyz: Pyrophosphate-extractable

[b] Ox: Oxalate-extractable

[c] DCB: dithionite-extractable counterparts

[d] 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_2, -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}C solid state Nuclear Magnetic Resonance (^{13}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 mL g^{-1} for abamectin and 30–150 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 ($R^2 = 0.91$, $p < 5\ 10^{-8}$) 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 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 cm^{-1} and band B: hydrophilic components, 1,647–1,633 cm^{-1}) was found and reported ($R^2 = 0.66$). Based on the derived model, $K_{OC} = 22{,}757 + 4{,}364$ A/B $-1{,}564$ 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 mL g^{-1} for tebuthiuron and from 0.4–0.6 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}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 $\mathrm{g}^{(1-1/n)}\,\mathrm{L}^{1/n}\,\mathrm{kg}^{-1}$.

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 Al^{3+}, Fe^{3+}, Fe^{2+}, Mg^{2+}, Ca^{2+}, Na^{+}, and 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^{-1} and 0.4–0.6 mL g^{-1}, 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 $K_{\mathrm{d.mineral}}$ 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 $K_{\mathrm{d.mineral}}$ contributed between 15 and 40% to the $K_{d\ \mathrm{average}}$ 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-Liébana 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^{-1} and that of tebuconazole from 2.4 to 47.4 L kg^{-1}.

Based on the regression equation that was proposed Gao et al. [231] for the sorption prediction of pymetrozine on six different soil samples: $\log K_F = 4.3708–4.5709 \times \log$ (pH in 0.01 mol·L^{-1} CaCl_2) + $0.4700 \times \log$ OC % + $0.0057 \times$ sand (%) + $0.0022 \times$ 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^+, $–CONH_2$, $-OH$, $–NHCOR$, $–NH_2$, $–OCOR$, and $–NHR$ [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, quinoxyfen, and triadimefon), and six neutral (α-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-Liébana et al. [138] evaluated the adsorption behavior of six different pesticides (α-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 (qe) 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 $\mu g\ L^{-1}$ or $\mu g\ kg^{-1}$) and therefore pose a higher ability to threat 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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Plant Uptake of Pesticide Residues from Agricultural Soils

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Contents

Abstract During recent decades, agriculture production has intensified by using a large number of chemical substances as pesticides to protect crops from unwanted fungi, weeds, and insects. It has been reported that long-time exposure of pesticides to different environmental conditions results in persistence of many derivatives of them in the environment. Intense global environmental issues have been raised due to the uptake of those pesticide residues present in agricultural soils by non-target organisms and planted crops. Indeed, the movement of such pesticide residue chemicals through the food chain may still cause potential health risks to humans.

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However, uptake of pesticide residues is more complicated and many factors have promoted the process. The uptake process and bioavailable concentrations of pesticide residues can highly differ depending on environmental conditions, characters of the planted crops, and physicochemical properties of the pesticides. Meanwhile, this chapter summarizes the pesticide residue types and their fate in the agricultural soils, highlighting the mechanisms as well as influencing factors for the plant uptake. Field-based investigations under natural conditions are required for future researches to make reasonable risk predictions for human health.

Keywords Agrochemicals, Factors, Human risk, Mechanisms, Persistence

1 Introduction

A wide range of chemical compounds is extensively used as pesticides around the world in agriculture to eradicate undesired pests from the cultivations [1]. Pest is a generous word to describe any creature like insects, plant pathogens, weeds, molluscs, birds, mammals, nematodes that have harmful undesirable effects on crops or livestock [2]. It was estimated that annual worldwide pesticide consumption was 2.7×10^6 tons [3]. Numerous groups of pesticides, which have different chemical and physical properties from one to another, are continuously used in agriculture. Depending on the function and the target organism, pesticides are categorized into various classes including insecticides, herbicides, fungicides, rodenticides, bactericides, algaecides, nematicides, molluscicides, ovicides, etc. [1, 2, 4]. However, among them insecticides, herbicides, fungicides and rodenticides utilize commonly in agriculture [2]. Insecticides are widely used to repel or kill insects in all stages of their growth cycles, while fungicides are used against the fungi and fungal spores, which have the potential to damage high crop yield. Further, herbicides are destroying weeds and other plant species that germinate where they are not wanted. Rodenticides are used to control rodents like mice, rats, woodchucks, beavers whereas they are usually formulated as baits [4]. Besides, they play an important role in preventing the spread of vector-borne diseases in the field.

Moreover, depending on the chemical materials involving in the pesticide manufacturing they can be either inorganic or organic. Pesticides such as copper sulphate, ferrous sulphate and sulphur are simple products that do not contain carbon in their chemical structure hence, they are called inorganic [5]. Comparably, organic pesticides like captan, pyrethrin, and glyphosate are based on chemicals having carbon as the active ingredients. Many feasible ways (modes of entry) are unique for each type of pesticide to enter into target pests such as systemic, contact, stomach poisons, fumigants, and repellents. Some pesticides are ingested to the pest from the mouth and transferred to the rest of the body, heading it to death. In fact, pesticides like malathion are able to attack the larval stomach and kill it [2]. Besides, some pesticides are only effective on target pests, when chemicals are physically contacted with the epidermis of the organism and entered through the lesion. Moreover, fumigants are forming poisonous vapour and transmitted via the respiratory system of pests which also leads them to death by poisoning.

Despite the beneficial outcome of using pesticides, inappropriate application of those chemicals over few decades may result in soil and water contamination by pesticide residues. Some mechanisms such as photochemical oxidation, photolysis, hydrolysis, and metabolism lead to pesticide degradation while resulting in residue products [4, 6]. Such residues, which are ubiquitous in the agricultural soils, are a major concern as they can persist for a long period in the environment. Pesticide residues contribute to the contamination of aquatic environments and eventually could adversely affect aquatic species. On the other hand, pesticide residue products may have much higher toxicity than the original pesticide even on the non-target organisms. Most importantly, pesticide residues can be uptaken by the non-target edible crops, which will grow in the following seasons [3]. In fact, pesticide residues derived from agricultural soils are found to accumulate in plants at minute levels typically from ng kg^{-1} up to mg kg^{-1}. Interestingly, 16 different pesticide residues including *p,p'* – DDT, *p,p'* – DDE, *p,p'* – DDD, etc. were detected in agricultural soil samples whereas 11 pesticide residues from them were detected in flora samples according to the study done by Zacharia et al. [7] at a sugarcane plantation in Tanzania. It is clearly shown biota uptake is one of an ultimate destination of pesticide residues in the environment. Further, Neuwirthová et al. [3] found many pesticide residues in soils from arable lands in Czech Republic, which were used as plantation lands many years before. Interestingly, many pesticides including epoxiconazole, tebuconazole, flusilazole, prochloraz, and pendimethalin were detected at increased frequencies and/or concentrations in the soils [3]. Importantly, the transformation product (2-hydroxyatrazine) of atrazine, which was banned decades ago, was frequently reported as a contaminant of agricultural soils in arable lands [3, 8]. These findings are proving the information of the long-time persistence behaviour of pesticide residues in the soil environment [9]. Hence, it was unable to provide the real risk associated with it [3].

However, many parameters have been recognized as governing factors for the behaviour of pesticide residues in soil [10]. Basically, the physicochemical properties of a given pesticide are influencing the fate and binding nature of residues in soils. Further, environmental factors and plant physiology and genotype have a dominating influence on the residue uptake process by plants [11]. Consequently, plant uptake of pesticide residues can be capable of having deleterious effects on wildlife and perhaps human beings through the food chains [7, 12]. This chapter highlights the types of pesticide residues, fate, and plant uptake mechanisms in agricultural soils. The influencing factors for the process of pesticide residues uptake by plants are also discussed alongside their negative effects, particularly on human beings.

2 Potential Pesticide Residues in Agricultural Soils

2.1 *Pesticide Residue Types*

Most of the applied pesticides will spread and react with the environment. Pesticides and their degradation products, which remain on and in foods, are known as pesticide residues. Many types of these pesticide residues could be found in the environment. Accumulated concentrations of some pesticide residues in different plants and soils are shown in Table 1. These pesticide residues could be classified by considering many characteristics. As mentioned above, pesticides are categorized based on the nature of active ingredients, their mode of entry, the chemical composition, and the target pest organism and the function [2, 19].

The classification of pesticides based on their chemical composition reflects the chemical and physical properties and effectiveness of the pesticides [2, 19]. Typically, synthetic and plant-originated organic chemicals are widely used as pesticides, however, several inorganic chemicals are also practised as pesticides in the world [2]. Depending on the chemical composition of pesticides, four main groups of pesticides can be recognized such as organochlorines, organophosphorus, synthetic pyrethroids, and carbamates [20–22].

Organochlorine pesticides represent one of the initially synthesized pesticide groups, which are used in agriculture. Examples of commonly used organochlorines are heptachlor, endosulfan, chlordane, and dichlorodiphenyltrichloroethane (DDT) [23]. The residual effect of these pesticides on the environment could extend for a long time. For many years, organochlorine pesticides have been used, however, due to their long residual effect many countries have led to the use of alternative pesticides such as organophosphorus and carbamate pesticides, which have a lower residual effect [24, 25].

Due to having multiple functions, organophosphorus pesticides are included in a broad spectrum of pesticides in controlling pests. Also, these pesticides are biodegradable, have slow pesticide resistance, and have reduced environmental pollution [24]. Some of the commonly used organophosphorus pesticides can be listed as glyphosate, malathion, diazinon, acephate, phosmet, and parathion [2, 23]. Carbamates are structurally and functionally similar to organophosphorus pesticides and both pesticide types affect the nerve transmission of pests. Carbamates could be degraded easily with reduced environmental pollution [2, 19]. Examples for carbamates are carbofuran, aminocarb, carbaryl, aldicarb, and pirimicarb [23].

One of the safest organic pesticide groups for food crops is synthetic pyrethroids and these pesticides have longer residual effect and stability than natural pyrethrins. Also, the persistence of most synthetic pyrethroids is negligible and could break due to the light, while the toxicity to mammals and birds is low [2]. Commonly used synthetic pyrethroids are cypermethrin, deltamethrin, and cyhalothrin [23].

The pesticides are classified by indicating the target organism and emphasizing the pesticide activity. The pesticide classes can be specified as herbicides (e.g. glyphosate), insecticides (e.g. chlorpyrifos), fungicides (e.g. chlorothalonil),

Table 1 Accumulated concentrations of several pesticide residues in different soils and plants

Pesticide type	Concentration range		Plant type	Reference
	Soil µg kg^{-1}	Plant µg kg^{-1}		
Hexachlorobenzene (HCB)	0.125–0.167	ND–0.033	Potato varieties^a	[9]
	0.230–1.215	0.050–0.330	Carrot varieties^b	
α-Hexachlorocyclohexane β-Hexachlorocyclohexane Υ-Hexachlorocyclohexane	ND–87.0	ND–3.66	Potato varieties^a	[9]
	ND–8.06	ND–2.86	Carrot varieties^b	
	18.5–769.5 dw	1.7–384.7 dw	Radishes (*Raphanus sativus*)	[13]
	0.7–19.6	0.4–0.6 fw	Sweet potato	[14]
	2.76–17.06 dw	2.00–12.89	Mango leaves (*Mangifera indica*), sugarcane (*Saccharum officinarum*), and Guinea grass (*Panicum maximum*)	[7]
2,4’-DDT (o,p’-DDT) 4,4’-DDT (p,p’-DDT)	1.2–152.4	ND–3.9	Potato varieties^a	[9]
	0.5–207.8	0.11–47.76	Carrot varieties^b	
	583.2–2581.4 dw	36–1759.2 dw	Radishes (*Raphanus sativus*)	[13]
	1.02–2.0 dw	2.44–4.07	Mango leaves (*Mangifera indica*), sugarcane (*Saccharum officinarum*), and Guinea grass (*Panicum maximum*)	[7]
α-Endosulfan β-Endosulfan	1.23–13.36	ND–3.23	Potato varieties^a	[9]
	0.57–14.96	ND–6.16	Carrot varieties^b	
	1.34–13.51 dw	1.67–13.0	Mango leaves (*Mangifera indica*), sugarcane (*Saccharum officinarum*), and Guinea grass (*Panicum maximum*)	[7]
Aldrin	0.001–12.66	ND–0.0019	Potato varieties^a	[9]
	1.6–4.3	0.013–2.900	Carrot varieties^b	
	1.11–5.66 dw	2.26–4.46	Mango leaves (*Mangifera indica*), sugarcane (*Saccharum officinarum*), and Guinea grass (*Panicum maximum*)	[7]
Endrin	0.33–31.0	ND–13.30	Potato varieties^a	[9]
	0.013–22.70	ND–7.320	Carrot varieties^b	
4,4′-DDE	783.9–1081.7 dw	56.9–809.5 dw	Radishes (*Raphanus sativus*)	[13]
	1.23–13.49 dw	1.96–11.56	Mango leaves (*Mangifera indica*), sugarcane (*Saccharum officinarum*), and Guinea grass (*Panicum maximum*)	[7]

(continued)

Table 1 (continued)

Pesticide type	Concentration range		Plant type	Reference
	Soil μg kg^{-1}	Plant μg kg^{-1}		
	–	9.47–12.95	Leaf vegetables (spinach – *Spinacia oleracea*, cabbage – *Brassica oleracea*, lettuce – *Lactuca sativa*, dhania – *Coriandrum sativum*, celery – *Apium graveolens*, parsley – *Petroselinum Crispum*, and kale – *Brassica oleracea*)	[15]
	–	9.07–12.75	Root vegetables (carrot – *Daucus carota*, cauliflower – *Brassica oleracea*, radish – *Raphanus raphanistrum*, broccoli – *Brassica oleracea*, turnip – *Brassica rapa*, Leek – *Allium ampeloprasum*, and spring onion – *Allium cepa*)	
Imidacloprid	–	1.37×10^3–410×10^3 dw	Rice plants (*Oryza sativa* L.)	[16]
	–	0.18×10^3–2.64×10^3	*Brassica rapa* L. varieties	[17]
Thiamethoxam	–	3.19×10^3–265×10^3 dw	Rice plants (*Oryza sativa* L.)	[16]
Difenoconazole	–	0.23×10^3–79.1×10^3 dw	Rice plants (*Oryza sativa* L.)	[16]
Clothianidin	0.02×10^3–0.5×10^3	0.07×10^3–7.0×10^3	Rice plants (*Oryza sativa* L.)	[16]
Chlordecone	–	0.8–262.7 dw	Radish plants	[18]

ND Not Detected, *dw* dry weight, *fw* fresh weight

[a] Potato varieties – Cara, Valour, Kestrel, and Desiree

[b] Carrot varieties – Nairobi, Major, and Autumn Kings

rodenticides (e.g. warfarin), bactericides (e.g. copper complexes), larvicides (e.g. methoprene), virucides (e.g. scytovirin), nematicides (e.g. aldicarb), molluscicides (e.g. metaldehyde), algaecides (e.g. copper sulphate), acaricides (bifenazate), termiticides (e.g. fipronil), lampricides (e.g. trifluoromethyl nitrophenol), and ovicides (e.g. benzoxazin) [19, 26].

Herbicides are used in agricultural fields to control weeds without harming the crop (selective herbicides) or control all the vegetation (total herbicides). These pesticides could be absorbed through roots or leaves, respectively, into the plants and the pesticide selectivity may depend on the differences in plant uptake, metabolism, and translocation mechanisms. Herbicides are classified based on their chemical composition. For example, glufosinate and glyphosate (organophosphorus herbicides), molinate and propham (carbamate herbicides), dicamba and chloramben (benzoic acid herbicides), alachlor and propanil (amide herbicides), and pyridate and norflurazon (pyridine and pyridazinone herbicides) can be presented [27].

Insecticides are applied to soil or plants to control pests such as insects in the crops. Insecticides also could be grouped according to the chemical composition, such as DDT and endosulfan (organochlorine insecticide), chlorpyrifos and fenitrothion (organophosphorus insecticides), methomyl and carbaryl (carbamate insecticides), permethrin (pyrethroid insecticide), and acetamiprid (neonicotinoid insecticide) [27, 28].

Fungicides are used in agriculture to protect fruits, vegetables, and cereals from fungal diseases [29]. Fungicides are classified according to their chemical composition. Examples of commonly used fungicides are chlorothalonil (organochlorine fungicide), fenpropimorph (morpholine fungicide), thiabendazole (benzimidazole fungicide), and cyproconazole (azole fungicide) [28].

2.2 Fate and Transport in Soil

As mentioned above, most of the applied pesticides on the plants or the soil would be dispersed in the surrounding environment. Even the pesticide application area is comparatively small, eventually, pesticides may spread into a larger area by adsorption into the soil, volatilizing into the air, or dissolving in water. Soil-applied pesticides may lead to unintended dispersal and non-target contamination in soil and surface water bodies through pathways such as surface runoff and flooding [30]. Further, groundwater and lower soil layers may be contaminated through percolation [2]. After the pesticide application, the fate and behaviour of the deposited pesticides on soil and plant surfaces may be influenced by many factors such as volatilization, adsorption, photochemical decomposition, chemical decomposition, microbial decomposition, movement, and organism uptake [31–33]. Physically, the soil has a heterogeneous nature while the soil structure varies laterally and vertically resulting in a complex water flow through the soil profile. Soil properties, pesticide properties, and environmental conditions determine the pesticide movement rate through the soil [34].

Adsorption plays a major role in affecting the interactions taking place between soil colloids and pesticides, because it directly or indirectly influences the extent of the other affecting processes [35]. Adsorption is the association of an atom, ion, or molecule from a dissolved solid, liquid, or gas to a surface. The adsorption of pesticides onto soil surfaces depends on many factors such as physicochemical characteristics of the adsorbent and the adsorbate, soil reaction, surface acidity, and temperature. In the case of the physicochemical characteristics of the adsorbent, the surface area and the total charge are more important than the surface charge density in most situations. When considering the physicochemical characteristics of the adsorbate, the adsorption process may be subjected to the water solubility, acidity and basicity of the molecule, shape and configuration, size of the molecule, polarity, charge distribution, and polarizability. The properties of adsorbent and adsorbate are influenced by the soil reaction in the clay-water system. Also, the degree of attachment and separation of adsorbate would be determined by the soil solution pH. The surface acidity as an important property in the soil system determines the adsorption and desorption of organic compounds. The temperature of soil systems may affect the adsorption processes since adsorption is an exothermic process, while desorption is an endothermic process. Distinct adsorption mechanisms could be identified as physical adsorption, chemical adsorption, and hydrogen bonding. As a result of short-range dipole–dipole interactions, van der Waals forces could be created between adsorbent and adsorbate to form physical adsorption. Mechanisms such as ion exchange could lead to chemical reactions between adsorbent and adsorbate to form chemical adsorption [34, 35].

The behaviour, distribution, and fate of pesticides could be strongly influenced by the physical and chemical properties of soil [36]. Topsoil is the area where pesticides could frequently be found [37]. Soil constituents with highly reactive surfaces mainly determine physical and chemical properties. These constituents could be divided into two fractions as the mineral fraction and the organic fraction. Crystalline clay minerals and amorphous and crystalline oxides/hydroxides represent the mineral fraction, while humic acid represents the organic fraction. Humic acid has a higher cation exchange capacity than clay minerals, because functional groups such as amino, carboxyl, phenolic hydroxyl, and alcoholic hydroxyl in humic acid contribute to form hydrogen bonds with pesticide molecules [35]. As an example, Yu et al. [33] showed that the adsorption and desorption processes of three pesticides, namely chlorpyrifos, myclobutanil, and butachlor were strongly controlled by soil organic matter (OM).

The pesticide mobility could be controlled by many factors related to the soil such as vegetation, preferential flow, soil moisture, amendment, soil tillage, and facilitated transport. The OM resulted from vegetation could adsorb hydrophobic pesticides through van der Waals forces, while phenolic hydroxyl and carboxyl groups in the OM could form hydrogen bonds with hydrophilic pesticides [34]. The transport of pesticides in the soil may occur through the downward and upward moving water, through the diffusion in soil airspace, and through the diffusion in soil water. Relatively non-volatile pesticide movement could be happened through percolating water, while air diffusion is more important in high volatile pesticide movement. In high evapotranspiration present areas, the upward movement of pesticides could be a factor [35]. Eventually, diffused or transported pesticides would be partitioned in the soil matrix.

The release of pesticides into the soil solution is identified as leaching. It could be resulted from the pesticide dissolution from an original form or through the pesticide desorption from soil surfaces. The leaching of pesticides is determined by the pesticide properties (sorption, degradation, and solubility) and soil properties (type, texture, and structure) [34, 38, 39]. For example, the leaching of nicosulfuron herbicide from clay minerals is strongly limited due to the rapid sorption [40]. Furthermore, due to the low degradation rate and low mobility, mesotrione has no movement lower than 20 cm in soil [41]. Pesticide leaching is strongly influenced by the soil type while pesticide properties have a partial contribution [26]. Also, leaching could be influenced by the soil moisture level and the evapotranspiration ratio. Both soil texture and structure could affect the pesticide movement and leaching because the degree of pesticide leaching is high in light-textured soils than in heavy-textured soils and the changes in soil texture usually affect the changes in soil structure. Due to the small-diameter pores in the high clay content soil, the molecular diffusion of pesticides may be restricted [35]. The fate of pesticides in the soil strongly determined by the climatic parameters such as appearance time of the first rainfall after pesticide application and the intensity and duration of the rainfall event [42].

Another important process for controlling the transport of pesticides and their residue levels in the soil is the degradation of pesticides. As mentioned above, pesticides could be degraded photochemically, chemically, or biologically [43]. Processes such as photolysis, photochemical oxidation, hydrolysis, and metabolism are contributing to the overall degradation of pesticides [12]. According to Si et al. [44] and van der Linden et al. [45], the degradation could be pH-dependent for certain pesticides which are susceptible to dissociation and hydrolysis. Soil microorganisms play an important role in pesticide degradation [46, 47]. The rhizosphere which has high biomass and microbial activity enhances pesticide degradation [34]. Pesticides could be degraded inside plant tissues either by enzymatic reactions of the plant [48] or due to activities of endophytic bacteria [49]. An example of abiotic pesticide degradation is the degradation of atrazine to form hydroxyatrazine and according to Wang et al. [50], this conversion is catalysed by the soil colloidal surface Bronsted acidity.

Soil macro-organisms such as earthworms could accumulate some pesticide residues in their bodies [24]. Usually, the uptake of pesticide residues such as myclobutanil and butachlor by earthworms is increased with the decreasing amount of soil OM. Pesticide residues could be accumulated in earthworm bodies via two pathways such as passive diffusion through the earthworm dermis and contaminated soil ingestion [51]. Due to the strong sorption of chlorpyrifos pesticide onto soils, earthworms are incapable of accumulating the pesticide from the soil surface via their dermis [33]. Besides soil macro- and micro-organisms, pesticides and pesticide residues could be degraded, translocated, and accumulated in plant tissues. The process involved in pesticide movement into vegetation is identified as plant uptake.

3 Mechanisms of the Uptake, Translocation, and Bioaccumulation of Pesticide Residues in Plants

Food crops and other plants in the environment are vulnerable to pesticide residue contamination. Pesticides remaining in the air and soil can be absorbed by plants through the plant aerial parts (leaves, fruits, and shoots) and roots, respectively (Fig. 1) [12, 52]. Herbicides are absorbed into plants through both leaves and roots, while some other organic pollutants are absorbed into plants only through roots from soil [53]. Organic pesticides are less volatile and their uptake into plants is generally happening through the plant root because usually it is the first tissue that soil pesticides come in contact with [53, 54]. Pesticide uptake from plants occurs in two processes, namely passive uptake and active uptake [52, 55]. In the passive uptake process, pesticide molecules are diffused into the plant roots in the direction of a reducing chemical potential within several plant components [52, 55]. For example, passive uptake is the major process of uptake of fungicides (e.g. imazalil and tebuconazole), herbicides (e.g. phenylurea), and insecticides (e.g. o-methylcarbamoyloxime) [55]. In the active uptake process, pesticide absorption occurs for some organic pesticides (e.g. phenoxy acid herbicides) against a chemical potential gradient with the assistance of carriers in root cell membranes

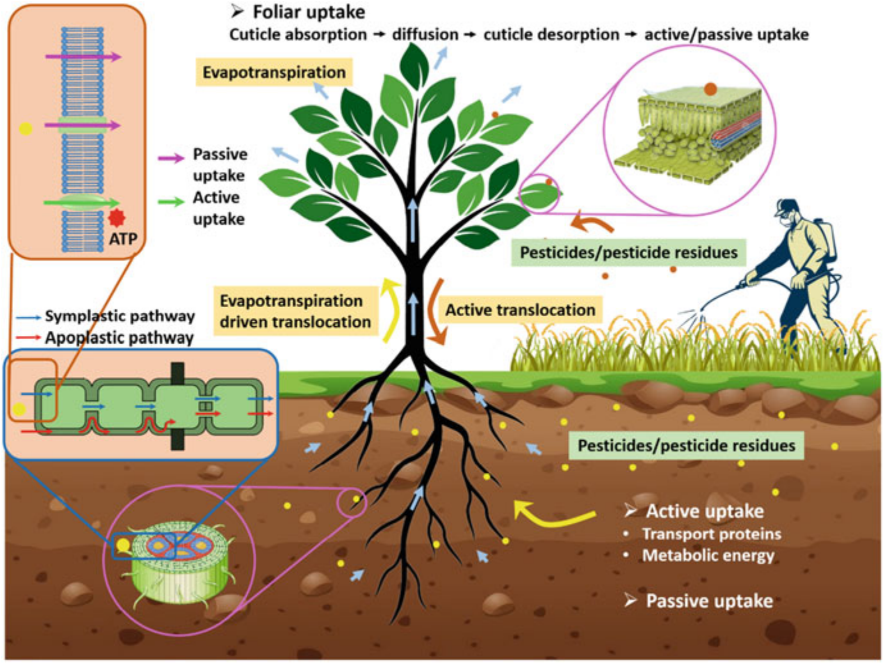

Fig. 1 Mechanisms of the uptake, translocation, and bioaccumulation of pesticide residues in plants

[52]. Transport proteins on the cell membrane and energy metabolism are key components in the plant root uptake [54]. The efficiency and degree of pesticide uptake from the soil is depending on the factors such as pesticide concentration in soil, physicochemical properties of pesticides, interaction between soil microorganisms and pesticides, plant species, exposure time, temperature, and other system variables [18, 56, 57].

Organic pesticide residue movement from soil to plant and translocation of them are primarily driven by the evapotranspiration process in the plants [55]. Contact pesticides neither penetrate the plant tissue nor translocate via the vascular system of the plants. Also, partially soluble organic pesticides are usually accumulated in plant roots due to the difficulty of moving to the shoots. Pesticides such as systemic herbicides (e.g. glyphosate) can be absorbed into plants and translocated into untreated tissues. This pesticide movement in plant tissues could be multidirectional or unidirectional which means that some pesticides can be moved either downwards or upwards in the plant while other pesticides can only move upwards [2]. The pesticide movement through plant tissues happens via two pathways, namely the symplastic pathway and apoplastic pathway. The symplastic pathway is identified as the route which lies through the protoplasts of the plant cortex, while the apoplastic pathway represents the route via the intercellular space and cell walls of the plant cortex [58–60]. According to previous studies, the uptake and translocation pathways of pesticides can differ depending on the physicochemical characteristics of pesticides and plants. Therefore, polar organic pesticides (e.g. atrazine, imidacloprid, and carbendazim) are most likely to be translocated via symplastic pathway, whereas non-polar organic pesticides (e.g. propiconazole and phenanthrene) are usually being translocated through the apoplastic pathway [54, 61]. Further, physicochemical properties of these molecules determine their long-distance transportation pathway inside the plant. For example, small organic molecules transported through either xylem or by phloem, whereas large organic molecules with low membrane permeability will be transported via phloem [53].

The lipid content of plant roots has a crucial role in organic pesticide uptake and storage because high lipid content leads to elevated uptake of hydrophobic organic pesticides [52, 54]. As mentioned in Ju et al. [62], the hydrophobicity and subcellular fraction concentration factor (SFCF) of pesticides determine their bioconcentration in plant roots. The SFCF reflects the ratio between pesticide concentration in total plant solid-phase components (root cell organelles and cell walls) and the water-soluble root cellular components (cell organelles and cell walls). It has been observed that organochlorine pesticides such as chlordecone insecticide can be translocated in plants (i.e. radish) via different routes. One route is the root absorption followed by evapotranspiration-driven translocation through diffusion from xylem vessels and the other route is the periderm adsorption followed by diffusion towards underlying tissues [18]. Lipophilic pesticides prefer diffusion through the periderm than root absorption. Also, chlordecone contamination is facilitated by organic acids produced in courgette roots through pesticide desorption from soil [18, 63].

Pesticides could be taken up through foliar parts of a plant and plant cuticle plays a major role in this process by acting as a potential barrier for pollutant penetration. A plant cuticle is a complex extracellular structure that covers the external surface of the plant's aerial parts. The behaviour of pesticide drops on plant surface could be influenced by the cuticle physicochemical properties and ultimately it affects the efficiency and rate of penetration. This penetration is a diffusion-controlled process that consists of three parts such as absorption into the cuticle, diffusion through it, and desorption from it. Cuticle hydration can increase the hydrophilic compound penetration, while hydrophobic compound transportation through the cuticle could be enhanced by factors that decrease wax viscosity [64]. When pesticides (e.g. chlorantraniliprole (CAP)) reach the apoplast of the leaf through cuticle and epidermis penetration, further they could penetrate the symplast through the plasma membrane with the involvement of carrier-mediated transportation (amino acid transporters) [65]. Active translocation of foliar uptaken pesticides can occur through phloem tissues to stems and roots. When pesticide uptake is high, crosswise diffusion of pesticides could be happening from phloem to xylem. These processes can be driven by diffusion resulted from concentration difference or transpiration [65]. These processes ultimately lead to pesticide residue accumulation in different parts of plants such as leaves, fruits, seeds, stems, roots, and tubers.

Bioaccumulation of organic pesticide residues in plant tissues can depend on the physicochemical properties of the pesticide such as lipophilicity and low water solubility. Increment of these factors may increase the bioaccumulation of the pesticides because non-polar contaminant molecules are less soluble in water while they can dissolve in plant lipids. The size of the contaminant molecule also important in the pesticide accumulation because the passage capability through biological membranes is increasing with the decreasing molecule size. The low biodegradability of the pesticides also leads to bioaccumulation in plant tissues. The biodegradation process resulted from the plant metabolic activities acts as a counter-reaction for the bioaccumulation by changing the chemistry of the pesticides [66].

According to many previous studies, the presence of pesticide residues in food items was in quantifiable amounts. Organophosphate and carbamate pesticide residues such as chlorpyrifos, 3-hydroxyl carbofuran, and methiocarb have been detected in considerable amounts in food samples in Nigeria. The comparison of pesticide residue presence between cereals, fruits, and vegetables indicated that cereals had much lower residue than in fruits and vegetables. Vegetables had the highest pesticide residues and the surface area to size ratio could be the reason for the relatively high contamination of vegetables [67].

4 Factors Influencing the Uptake of Pesticide Residues by Plants

The factors affecting the uptake of pesticide residues from the soil by plants are of great importance, especially for the health of herbivores and/or human. As shown in Fig. 2, several factors are recognized, which influence the pesticide residues uptake through roots and the translocation to the aerial parts of plants or accumulation in plant roots grown under irrigated soils in real agricultural systems [13, 68]. Basically, predicting the uptake of pesticide residues from agricultural soil by plants is complex hence, environmental factors, plant physiology factors, and physicochemical properties of pesticide residues or a combination of these are effective for the uptake of residue into plants.

4.1 Environmental Factors

In general, properties of the agricultural environments (i.e. soil, climate) largely shape and determine the uptake and accumulation of the pesticide residues by crop plants [69]. Furthermore, the magnitude of bioavailability/bioaccessibility of pesticide residues within the rhizosphere plays a vital role in plant uptake. It has been

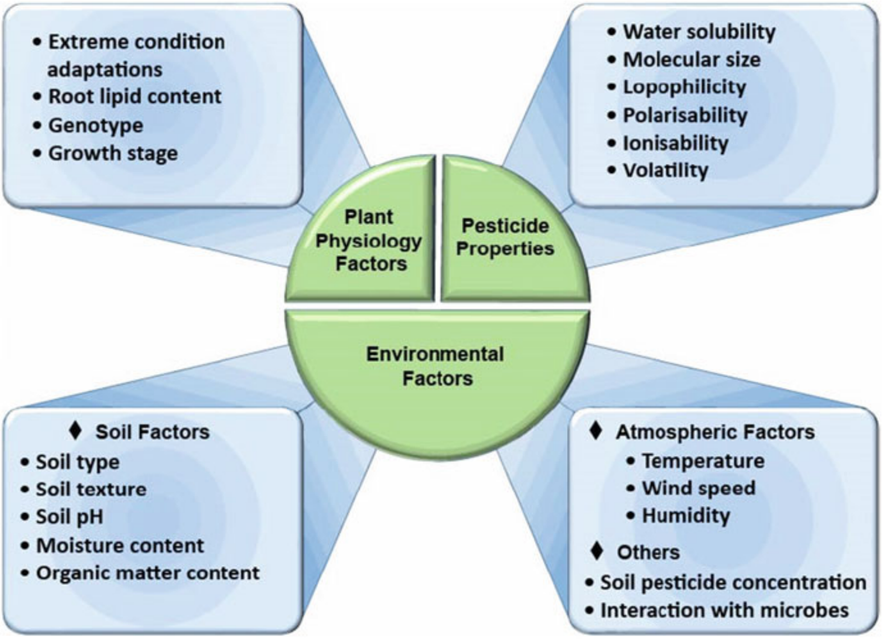

Fig. 2 Factors influencing the uptake of pesticide residues by plants

previously proven that the crops grown in sandy soils with a lower proportion of OM and clay have a higher potential to uptake pesticide residues than in soils enriched with clay and OM [11]. Moreover, soil texture can also have a huge impact on the persistence of pesticide residues in soil and plant uptake [69]. For example, loamy soil texture is responsible for limiting the bioavailability of pesticide residues in the soil thus, leading to reduced plant uptake. Whereas, Xu et al. [70] have argued that sandy soils are capable of fast infiltration and percolation of contaminants thus providing less bioavailability of pesticide residues around the rhizosphere. Moreover, higher humic acid content, a major component of soil, can influence the bioavailability of pesticide residues in the soil. In addition, soil pH can also have a huge influence on the uptake of pesticide residues by plants [57]. Biodegradation of pesticide residues is increased at the alkaline pH by limiting their bioavailability in soil. In fact, the acidic pH of soil usually favours the sorption of the pesticide residues onto the soil, while impacting positively to the uptake of residues by plants [11]. However, acidic soil facilitates the formation of neutral form of residues thus, giving the appropriate conditions for the plant uptake [11]. Furthermore, crops growing in well-aerated soils (under aerobic conditions) compared to compacted and waterlogged soils may have higher potential to upgrade the functionality of roots in the rhizosphere, while enhancing the ability of the uptake of pesticide residues through water and nutrients [11, 71].

In addition to the aforementioned factors, ambient temperature, wind speed, and air humidity can also act as influencing factors for the uptake and accumulation of pesticide residues into crop plants. High temperature, high wind, and low humidity of the environment positively shape the evapotranspiration rate of plants thus facilitating enhanced pesticide residues uptake. It is highlighted that agricultural sites located in dry and hot climatic regions compared to cold or humid regions highly favour pesticide residues uptake from soil. Furthermore, owing to the high temperature, vapour pressure, and volatility of pesticide molecules are noticeably altered which results in increased evapotranspiration rate leading to the plant uptake [72]. Whereas, in the case of crop plants grown under adequate soil moisture conditions, the evapotranspiration rates are expected to exhibit excessive potential for pesticide residues uptake. However, it was reported that plants grown in outdoor agricultural lands accumulate fewer residues compared to the plants grown under greenhouses, which might be due to the pesticide exposure to some particular environmental conditions like air currents, photodegradation, and soil dispersion [57, 73].

4.2 Plant Physiology Factors

Generally, plant physiology properties have a decisive role in the overall uptake from the soil and translocation through the plant, nevertheless, the process driven by transpiration is also plant-specific. In addition, as uptake of residues from the soil is inextricably linked to the evapotranspiration process, there are some adaptive mechanisms of plants to minimize transpiration rate [74]. Most importantly, the plants grown in drought conditions (under stress) exhibit less potential for residue uptake from soil, because they have evolved many mechanisms for reducing consumption of resources compared to the plants exposed to the optimum conditions. Therefore, various defence mechanisms, such as stomatal closure, hormone regulation, antioxidants generation, induction of stress proteins, and osmotic adjustment, have been found in plants to cope with such adverse abiotic environmental conditions [75–77]. Moreover, the genotype of the plant is affecting the potential for pesticide residues uptake [68]. It was found that the uptake ability of pesticide residues is exerting different patterns within the crop plant varieties even belonging to the same genus [78]. Furthermore, the accumulation of residues in plants from soil may vary according to their different growth stages as seedling stage (S-stage), rapid growth stage (R-stage), and maturation stage (M-stage). The total amount of the insecticide imidacloprid taken up by leafy vegetables was investigated by Li et al. [17] whose results demonstrate that concentration of imidacloprid could increase with vegetative growth. Similarly, Ge et al. [16] compared the capacity of rice plants (*Oryza sativa* L.) to uptake and distribute imidacloprid (IMI) and thiamethoxam (THX) pesticides from soil and found out that the capability of accumulation of those pesticide residues is much greater in above-ground parts (IMI-10.0 and 410 mg kg^{-1} dw; THX-23.0 and 265 mg kg^{-1} dw) than in roots (IMI-1.37 and 69.3 mg kg^{-1} dw; THX-3.19 and 30.6 mg kg^{-1} dw). However, some previous studies reported that root crops like carrot, potato, beet, and radish have more susceptibility to accumulate residues of many organochlorines, such as DDT, chlordane, endrin, from agricultural soils to a greater extent [9, 68]. Interestingly, uptake concentration of organochlorine residues was noticed much higher in carrots compared to other root crops, such as radish, beet, potato, etc. [79]. In fact, leafy vegetables are highly vulnerable to uptake than succulent crops with small root system [11].

In addition, pesticide residues accumulation in root is governed by the plant root lipid content thereby, partitioning into the lipids is considered as primary sorption mechanism of poorly soluble pesticide residues [52, 80, 81]. The potential uptake of pesticide residues from agricultural soil into aerial parts of the plants highly differs depending on the growing season of crops. Crops that are growing during the rainy period do not favour the uptake of pesticide residues from soil, thus the summer season positively influences the uptake. Once these residues are taken up by the plant, they are translocated to aerial parts of the plant such as shoots, leaves, or fruits [82].

4.3 Physicochemical Properties of Pesticide Residues

The persistence of the pesticide residues in the environment and toxicity on non-targeted species depend upon several physicochemical characteristics of pesticides [7, 82]. Molecular size, ionizability, water solubility, lipophilicity, polarizability, and volatility act as dominating factors to determine the pesticide's interaction with the environment. The physical and chemical parameters of some selected pesticide residues are listed in Table 2. Long-time persistence (long half-life) of pesticide residues is not much desirable where residues can be uptaken via the root system of non-targeted species. Further, active adsorption of pesticide residues through the roots is influenced by the water solubility of residues [83]. Pesticides are available from high soluble to insoluble compounds. Solubility property is influencing the mobility of the residues in the soil environment. High soluble pesticide residues could dissolve well with rainwater and leach downwards while reducing the bioavailability around the rhizosphere [84]. Insoluble residues can be retained in soil whereby are adsorbed tightly on various inorganic and organic soil fractions for a long period.

In addition, lipophilicity denoted by octanol/water partition coefficient (log K_{ow}) is one of the most important physicochemical properties to screen pesticide translocation within the tissues of plants particularly through xylem [16, 85]. It is noteworthy that pesticide residues with high log K_{ow} values (>1.8) have weak translocation performance in plants [17]. Thus pesticide residues with low solubility usually can accumulate in the root system hence, very difficult to be transported to the aerial parts [69]. For example, pesticide IMI (log $K_{\mathrm{ow}} = 0.57$) and THX (log $K_{\mathrm{ow}} = -0.13$) were detected in high concentration in leaves rather than those in roots, while it was differing from the difenoconazole (log $K_{\mathrm{ow}} = 4.4$) residue which could have been attributed to their octanol/water partition coefficient [16, 52]. Moreover, it has been recognized that high molecular weight chemicals are difficult to be uptaken by plants than chemicals with lower molecular weight [72]. The basic chemical structure of the compound plays a critical role as it can influence the persistence of the pesticide in the soil. On the other hand, pesticide molecules in their ionic form might have increased desirability to be taken up by the plant in low soil pH condition [86]. Nevertheless, they are tightly bound to negatively charged soil fractions and persist for a year or more [87]. Moreover, most of the pesticides are easily broken down into another product, which can be either more stable or transient and complex than their parent compounds. Contrary to this, those newly evolved products may become less toxic chemicals. However, volatilization and photochemical transformation of pesticide residues are of particular interest, because they are among the factors affecting the uptake of the residue by plants [72, 88]. Pesticides with high volatility would completely disappear within a short period, hence reducing the presence of residue in the soil environment. Besides volatilization, pesticides are subjected to photochemical processes by exposing to UV radiation thus, the transformation of the structure is depending upon the complexity of the pesticide compound [88]. It was reported that about 80–90% of pesticides applied into the agricultural fields get volatilized within few days [86].

Table 2 Physicochemical properties of several pesticides that determine their translocation capacity within the plant

Pesticide	Activity	Formula	Octanol water partition coefficient (Log K_{ow})	Water solubility (mg L^{-1}) at 25°C except noted below	Molecular weight (g mol^{-1})
Imidacloprid	Insecticide	$C_9H_{10}ClN_5O_2$	0.57	510 (20°C)	255.66
Thiamethoxam	Insecticide	$C_8H_{10}ClN_5O_3S$	−0.13	4,100 (20°C)	291.71
Difenoconazole	Fungicide	$C_{19}H_{17}C_{12}N_3O_3$	4.4	3.3 (20°C)	406.3
Clothianidin	Insecticide	$C_6N_5H_8SO_2Cl$	0.905	327 (20°C)	249.678
Chlordecone	Insecticide	$C_{10}Cl_{10}O$	4.5	2.7	490.633
Chlordane	Insecticide	$C_{10}H_6Cl_8$	4.74	2.78	409.8
Aldrin	Insecticide	$C_{12}H_8Cl_6$	6.50	0.027	364.90
Endrin	Insecticide, rodenticide	$C_{12}H_8Cl_6O$	5.2	0.230	380.90
Hexachlorobenzene (HCB)	Fungicide	C_6Cl_6	5.73	0.005 (20°C)	284.8
Endosulfan	Insecticide	$C_9H_6Cl_6O_3S$	3.83	0.32 (22°C)	406.93
Dichlorodiphenyldichloroethylene (4,4’-DDE)	Insecticide	$C_{14}H_8Cl_4$	6.51	0.260	318.03
Dichlorodiphenyltrichloroethane (4,4’-DDT)	Insecticide	$C_{14}H_9Cl_5$	6.91	0.025	354.49
Dichlorodiphenyldichloroethane (DDD)	Insecticide	$C_{14}H_{10}Cl_4$	6.02	0.09	320.04
Malathion	Insecticide	$C_{10}H_{19}O_6PS_2$	2.75	145	330.358
α–Hexachlorocyclohexane (α-HCH)	Insecticide	$C_6H_6Cl_6$	3.08	2.00	287.86
β-Hexachlorocyclohexane (β-HCH)	Insecticide	$C_6H_6Cl_6$	4.14	31.40	287.86

(continued)

Table 2 (continued)

Pesticide	Activity	Formula	Octanol water partition coefficient (Log K_{ow})	Water solubility (mg L^{-1}) at 25°C except noted below	Molecular weight (g mol^{-1})
ϒ-Hexachlorocyclohexane (ϒ-HCH)	Insecticide	$C_6H_6Cl_6$	2.67	10.0	287.86
Glyphosate	Herbicide	$C_3H_8NO_5P$	−1.0	12,000	169.073
Trifluralin	Herbicide	$C_{13}H_{16}F_3N_3O_4$	4.69	<1 (27°C)	335.28

5 Major Impacts on Human Health and the Environment

The excess and widespread use of pesticides has triggered many environmental and health-related issues worldwide. As stated in Bhandari et al. [37], more than two million people living in developing countries have a higher health risk due to excessive pesticide use. Also, previous estimations stated that the annual death rate of pesticide poisoning was about 5,000–20,000 [2]. Many chemical pesticides and their residues released into the surroundings have led to environmental pollution. Specifically, pesticide residues can spread in soil, water, and air resulting in the increase of soil, water, and air pollution by reducing their quality. Ultimately, these pesticides and their residues can end up in the human body and may cause diseases especially in the renal, reproductive, nervous, respiratory, endocrine, immune, and cardiovascular systems [19, 89]. According to Golge et al. [28], pesticides may result in genotoxic, neurotoxic, and carcinogenic activities in the human body.

The degree of the harmful health impact of pesticides and their residues can be determined by the toxicity of pesticide chemicals, the magnitude of exposure, and the exposure time. Exposure is the contact of pesticide substance with the human body and it can happen through ingestion of contaminated water and food, inhalation of pesticide containing dust and air, and the direct dermal absorption of pesticides [2, 90]. When the pesticide exposure level surpasses the acceptable dosage level, harmful effects can take place in the human body [28]. The toxicity of pesticides can be either acute or chronic. Acute toxicity is defined as the capability of a chemical substance to cause harmful health effects right after exposure. This acute toxicity can occur from the pesticide exposure during the application, pesticide drift from croplands, accidental or intentional poisoning [91]. Chronic toxicity reflects the capacity of a chemical substance to generate harmful health effects during long-time exposure. This chronic toxicity can result from the pesticides and their residues containing in the harvest. Due to pesticide poisoning, many symptoms in the human body can appear such as nausea, headaches, faintness, body aches, weakened vision, skin rashes, and muscle cramps [2]. Many chronic effects caused by pesticide poisoning can be listed as different types of cancer, neurodegeneration, blood disorders, reproduction effects, birth defects, genetic alteration, endocrine disruption, and respiratory, digestive and renal problems [19, 92].

Pesticides that are significantly hazardous for humans are identified as priority substances. For example, herbicides such as atrazine, triazine, simazine, and terbutryn have been characterized as priority substances by the water policy directive draft by European Union (2013/39/EU) [93]. However, due to good weed controlling ability in crops such as cereal, cotton, and sugarcane these herbicides are currently being used extensively [94]. Carbamate pesticides are suspected as mutagenic and carcinogenic substances that can be enormously toxic to animals and humans [67]. As stated in Saini et al. [95], carbofuran is a toxic carbamate insecticide that can cause embryotoxic and teratogenic effects on humans through cholinesterase inhibition. Pesticides such as metalaxyl-M can possess low to moderate toxicity while acetamiprid insecticide causes relatively low toxicity in mammals [28]. Also, a study of chronic dietary exposure to pesticides in a Greek population showed that organochlorines and pyrethrins residues in vegetables and fruits caused negligible effects on humans [96].

According to many research findings, humans can be exposed to pesticides mainly via contaminated food ingestion [96, 97]. Analysis of dried brown beans and watermelons in Nigeria identified dichlorvos, chlorpyrifos, dimethoate, and diazinon pesticide amounts higher than the acceptable residue limits [67]. Many cowpeas, millet, soybeans, white pepper, egusi seeds, and maize samples collected from Cameroon had one or more pesticide residues of dimethoate, acetamiprid, imazalil, carbofuran, malathion, metalaxyl, and DDT higher than the European Union maximum residue limits [98]. Gherkin plant is susceptible to many insects, bacterial, and fungal infections and the samples analysed in Turkey showed the residues of applied pesticides such as metalaxyl, chlorothalonil, and acetamiprid [28]. Also, pesticides such as acetamiprid, aldicarb, carbofuran, metalaxyl, pirimicarb, carbaryl, and isoprocarb are often inspected in cucumber and Chinese cabbage samples in China [99].

Apart from the health effects to humans, pesticide residues can pose adverse effects on the environment as well. Extensive use of pesticides can intensify the soil accumulation of residues and ultimately it can affect the soil microorganisms and soil structure. The degradation products of pesticides can alter the biochemical reactions, microbial diversity, and enzymatic activities. Also, it may reduce soil fertility and soil biomass [2]. According to Chandran et al. [23], the toxicity of degradation products of pesticides is more toxic than the parent pesticide. Pesticides remaining in the soil for long periods can be a threat to the ecosystem by spreading via food chains [92]. Intensive pesticide application can lead to the increase of pesticide resistance of pests and also, it can affect non-target organisms in the environment [99]. For example, populations of pollinators, natural predators (important for pest control), and earthworms can be reduced by pesticides such as carbamates and some organophosphorus pesticides [24]. It has been reported that the volatilized herbicides can affect the primary producers by damaging non-target plants including some rare species [19]. Pesticides can accumulate and pollute surface water bodies through surface runoff, irrigation, leaching from treated soil, pesticide spray equipment washing, and accidental spillage [2]. Lv et al. [55] stated that tebuconazole fungicide can pose health effects on humans via aquatic organism contamination.

6 Future Outlook and Considerations

The rapidly growing population creates a demand in approximately 70% increment of food production worldwide. Anthropogenic chemicals are quite frequently using to control pest effects on crop production thereby remarkably increasing agricultural productivity [72]. Despite advances that have been made, excessive usage of pesticides leads to the introduction of pesticide residues to agricultural soils. Perhaps the most challenging part is the cultivation of safe crops using contaminated lands [100]. Laboratory experiments have proven enough that the soil acts as a primary sink for pesticide-based soil contaminants and uptake of them by various plant species. Pesticide residues accumulated in edible plants are of great concern due to the dietary ingestion of them via food chain can harm to human health. As the basis for the most food productions being linked with the soil quality, it is important to assess dissipation patterns and pathways of pesticides in agricultural ecosystem qualitatively and quantitatively. Even so, laboratory experiments are limited to few conditions, hence it may be difficult to predict the potential risk of plant uptake. Therefore, it is obvious to conduct studies under realistic field conditions to compensate for such limitations and to make reasonable risk predictions for human health which should be taken into account [53]. Further, the effect of the pesticides and the uptake of residues by plants may vary in different locations in the world. The statistics may significantly differ in the tropics compared to their counterparts in the temperate. Thus, comprehensive studies should be carried out in tropical and subtropical agricultural regions where intensive research has not been carried out yet in the field of ecotoxicology [101]. Additionally, introducing soil quality standards and prospective risk assessment schemes for commonly used pesticides will bring up control in pesticide application rate and thereby lowering the effect to the agroecosystems [101].

There are many different types of pesticides to manage the population of pests nevertheless, based on their coverage they can be either narrow-spectrum or broad-spectrum. In the future, it would be interesting to have an understanding of how that wide range of chemical mixtures in the field conditions influence plant uptake [102]. It is assumed that the association of botanical pesticides derived from the same essential oil may have synergistic as well as antagonistic effects on a selected pest and its ecosystem [103]. However, utilization of the same land for various seasonal plants has a risk for the production of safer agricultural crops, whereas uptake patterns of soil persistent pesticides are depending on the plant species. In the meantime, it is required to conduct experiments using different soil types with various textures to access the potential risk for plant uptake of pesticide residues. Perhaps, in some risk assessment studies calculate the bioconcentration factor (BCF) to measure the tendency of pesticide residues accumulation in crops. Very high BCF values suggest that uptake of residues from contaminated soil is increasing for the particular plant. However, the plant could accumulate residue from the mode of application thus BCF value is not suitable for all the situations to measuring the potential of plant uptake effect [104]. Importantly, proper eco-toxicological risk assessments should be undertaken at each stage of cropping to ensure safe food production thereby reducing health risks for humans [105].

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Contribution of Land Runoff to the Release of Pesticides into Water Bodies in Arable Areas

Paola Verlicchi and Andrea Ghirardini

Contents

Abstract The release of micropollutants into surface water bodies may be due to different pathways, including wastewater treatment plant effluent, combined sewer overflows and surface runoff. Many studies have dealt with the chemical characteristics of the first two types, whereas less attention has been paid to those of surface runoff in agricultural areas. Pesticides are the main micropollutants occurring in this stream and their impact on the receiving water body may be of great concern. In this context, the current chapter aims to provide a snapshot of the occurrence of common pesticides in the runoff of arable land and it discusses the main factors affecting their fate and behaviour once in the soil. Collected measured concentrations are compared with the corresponding predicted-no-effect concentrations in order to evaluate the potential risk due to surface runoff release into the receiving water body. It also presents some best practices that aim to mitigate their migration towards surface water. The chapter concludes with a focus on the main pesticides found in surface

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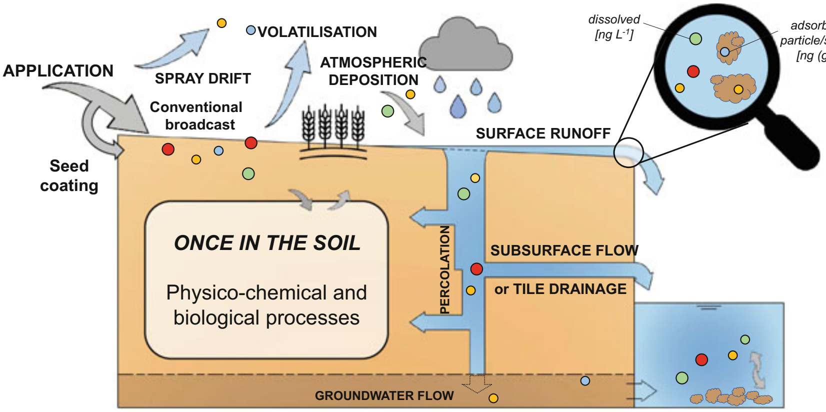
and groundwater in Italy, in particular in the Po Valley, and on the environmental risk posed by residues of a selection of pesticides in the surface water in two Spanish regions.

Graphical Abstract



Keywords Mitigation measures, Pesticides, Rural areas, Surface runoff, Water compartments

1 Introduction

Pesticides are applied in large amounts all over the world to protect crops from pests and indirectly increase their production. More than two million tonnes are used per year on a global basis, most of which are herbicides (50%), followed by insecticides (30%), fungicides (18%) and other types such as rodenticides and nematicides [1]. Focusing on European countries, data reported in the Eurostat database (https://ec.europa.eu/eurostat/) show that, in the period 2011–2019, sales of pesticides reached a maximum in 2016 (370,000 t) and then decreased over the following 3 years down to 333,000 t in 2019. The data also showed that fungicides and herbicides were the groups most sold and over two thirds of the sales volume refer to only four countries: Germany, Spain, France and Italy.

Once applied on the soil, pesticides are subjected to physical, chemical and biological processes as well as mobilisation within the soil and out of the soil (volatilisation) [2–4]. The presence of water in the soil favours their migration from the application point [5]. Most of the pesticides are characterised by their long persistence in the environment and concentrations of their residues are found in many surface water bodies and aquifers worldwide. Moreover, due to their persistence, they tend to accumulate in water compartments, soil and plants, biomagnificate in animal species tissues and enter the food chain [6]. High quantities of pesticides applied on rural land can damage microflora and microfauna in the soil and also interfere with the sorption properties of nutrients useful for plants in the soil [1].

Increasing attention is given to their potential negative effects on the environments. Environmental quality standards (EQS) have already been defined for some pesticides and specific ecotoxicological studies are currently being conducted on new substances and also on mixtures of pesticides. At EU level, dedicated directives have been set to promote and guarantee a sustainable use of chemicals including pesticides (2009/128/EC *Directive on the Sustainable Use of Pesticides*) [7]. In addition, the Watch List, introduced by Directive 2013/39 [8], defined by Decision 2015/495 [9], and updated by Decision 2018/840 [10] and Decision 2020/1161 [11], has to include substances "for which Union-wide monitoring data are to be gathered for the purpose of supporting future prioritisation exercises in accordance with Article 16(2) of Directive 2000/60/EC" [12]. Selected pesticides were always included on the first Watch List, and the recently updated list includes ten more substances: Dimoxystrobin, Famoxadone, Imazalil, Ipconazole, Metaflumizone, Metconazole, Penconazole, Prochloraz, Tebuconazole and Tetraconazole.

This study focuses on the occurrence of common pesticides in the runoff of arable land after their application and discusses the main factors affecting their fate and behaviour once in the soil. Collected measured concentrations (MECs) are compared with the corresponding lowest predicted-no-effect concentrations (PNECs) in order to evaluate the potential risk due to surface runoff release into the receiving water body. The study also presents some best practices that aim to mitigate their migration towards surface water. Some case studies are presented: focus is made on the main pesticides found in water compartments (surface and groundwater) in Italy, in particular in the Po Valley, the largest rural area in Italy characterised by a high amount of applied pesticides and on the environmental risks posed by residues of a selection of pesticides in the surface water in two Spanish regions.

2 Pesticides in the Environment and Compounds Included in the Study

A number of chemicals belonging to a broad spectrum of groups are applied on agricultural land for the treatment of pests and to increase crop production. Their application rate, method and calendar during the year may strongly affect their behaviour in the soil matrix. Once applied, pesticides are subjected to different processes, including mobilisation within the soil and runoff, after rain events. Many monitoring investigations pointed out the worldwide occurrence of most of the applied pesticides in the surface water adjacent to the rural areas where they were applied [13–15].

A list of some of the historic- and current-use pesticides commonly found in the aquatic environment adjacent to the rural areas is reported in Table 1, together with

Table 1 Pesticides included in this study, classified according to their target organism (Group) and their chemical family (Class) together with their main chemical, physical and toxicological properties

Compounds	Group	Class	Chemical formula	Molecular weight [g mol^{-1}]	Log K_{OW}[a]	Log K_{OC} [mL g^{-1}][a]	Water solubility (**20–21°C**) (*24–25°C*) [mg/L][a]	Persistence in soil – DT_{50} [days][a,b]	GUS	Lowest PNEC in fresh water [µg L^{-1}][c]	EU directives/ watch lists[d]
Atrazine	Herbicides	Triazines	$C_8H_{14}ClN_5$	215.7	2.61	1.6–2.2	**33**	42–75	3.5	0.6	2013/39
Azoxystrobin	Fungicides	Aryloxypyrimidines	$C_{22}H_{17}N_3O_5$	403.4	2.5	2.3–2.7	**6**	72–164	2.9	0.2	
Bromacil	Herbicides	Organobromides	$C_9H_{13}BrN_2O_2$	261.1	2.11	1.0–2.1	*700–1,287*	60	3.9	11.2	
Carbendazim	Fungicides	Benzimidazoles	$C_9H_9N_3O_2$	191.2	1.52	2.1–3.4	*1.5–8*	40–360	2.0	0.01	
Chlorpyrifos	Insecticides	Chloropyridines	$C_9H_{11}Cl_3NO_3PS$	350.6	4.96	3.0–4.5	*1.4*	7–120	−0.4	0.001	2013/39
Clothianidin	Insecticides	Neonicotinoids[e]	$C_6H_8ClN_5O_2S$	249.7	0.7–0.9	1.8–2.3	**327–340**	13–1,386	5.4	2.2	2015/495 and 2018/840
Diazinon	Insecticides	Pyrimidines	$C_{12}H_{21}N_2O_3PS$	304.4	3.81	2.3–3.2	*40*–**60**	7–40	1.4	0.005	
Diflufenican	Herbicides	Pyridinecarboxamide	$C_{19}H_{11}F_5N_2O_2$	394.3	4.2	3.5	*0.05*	44–248	1.1	0.009	
Dimethomorph	Fungicides	Morpholines	$C_{21}H_{22}ClNO_4$	387.9	2.68	2.6	**42–49**	10–75	2.3	5.6	
Diuron	Herbicides	Phenylureas	$C_9H_{10}Cl_2N_2O$	233.1	2.68	1.7–2.9	*37–42*	30–365	3.2	0.07	2013/39
Flonicamid	Insecticides	Pyridinecarboxamide	$C_9H_6F_3N_3O$	229.2	0.3	1.4	**5,200**	2–7	1.7	25	
Fluometuron	Herbicides	Phenylureas	$C_{10}H_{11}F_3N_2O$	232.2	2.42	1.8	111[f]	64–86	4.1	0.3	
Fluopicolide	Fungicides	Benzamides	$C_{14}H_8Cl_3F_3N_2O$	383.6	2.9	2.5	**3**	132–561	3.8	0.1	
Glyphosate	Herbicides	Phosphonoglycines	$C_3H_8NO_5P$	169.1	−3.4	2.9–4.7	**11,600**	1–133	−0.7	28	
Imidacloprid	Insecticides	Neonicotinoids	$C_9H_{10}ClN_5O_2$	255.7	0.57	2.1–2.9	**610**	104–229	3.0	0.008	2015/495 and 2018/840

Iprovalicarb	Fungicides	Carbamates	$C_{18}H_{28}N_2O_3$	320.4	3.2	2.0	**17.8**	15	2.4	0.9	
Linuron	Herbicides	Phenylureas	$C_9H_{10}Cl_2N_2O_2$	249.1	3.2	2.7–3.0	*75*	56–175	2.3	0.1	
Mesotrione	Herbicides	Sulphones	$C_{14}H_{13}NO_7S$	339.3	0.1-0.9	1.3–2.1	**15–22**	7–32	2.8	0.2	
Oxyfluorfen	Herbicides	Diphenyl ethers	$C_{15}H_{11}ClF_3NO_4$	361.7	4.86	3.9	*0.1*	73	0.2	0.4	
Pendimethalin	Herbicides	Dinitroanilines	$C_{13}H_{19}N_3O_4$	281.3	5.20	3.8–4.6	**0.33**	90–120	−0.8	0.02	
Permethrin	Insecticides	Pyrethroids	$C_{21}H_{20}Cl_2O_3$	391.3	6.5	4.1–4.9	**0.01**	40	−1.1	0.0002	
Prochloraz	Fungicides	Imidazoles	$C_{15}H_{16}Cl_3N_3O_2$	376.7	3.53	3.1–3.9	**0.02**	15–556	0.7	0.2	2020/1161
S-metolachlor	Herbicides	Chloroacetanilides	$C_{15}H_{22}ClNO_2$	283.8	3.0–3.4	2.0–2.5	*488*–**530**	12–90	2.9	0.2	
Tebuconazole	Fungicides	Triazoles	$C_{16}H_{22}ClN_3O$	307.8	3.7	2.9	**36**	20–92	1.9	0.2	2020/1161
Tebufenozide	Insecticides	Carbohydrazides	$C_{22}H_{28}N_2O_2$	352.5	4.25	4.5	*0.83*	52–115	−0.9	0.2	
Terbuthylazine	Herbicides	Triazines	$C_9H_{16}ClN_5$	229.7	3.4	2.2–2.7	**5**–*9*	22–75	2.5	0.06	
Terbutryn	Herbicides	Triazines	$C_{10}H_{19}N_5S$	241.36	3.74	2.5–4.6	**25**	14–77	−0.5	0.06	
Tetraconazole	Fungicides	Triazoles	$C_{13}H_{11}Cl_2F_4N_3O$	372.1	3.56	2.7–3.3	**150**	136–1,688	2.7	0.3	2020/1161
Thiamethoxam	Insecticides	Neonicotinoids	$C_8H_{10}ClN_5O_3S$	291.7	−0.13	1.7	*4,100*	50	3.9	2.9	2015/495 and 2018/840
Triadimenol	Fungicides	Triazoles	$C_{14}H_{18}ClN_3O_2$	295.8	3.18	2.4	**120**	110–375	3.8	3.2	
Transformation products (TP)[g]											
Aminomethylphosphonic acid (AMPA),			CH_6NO_3P	111.0	−1.63	3.0–4.4	**146,600**	23–958	−0.3	79.7	
Atrazine desethyl desisopropyl			C3H4ClN5	145.5	0.32	1.7	600[f]	14–68	3.7		
Deethylatrazine (DEA)			$C_6H_{10}ClN_5$	187.6	1.5	1.8	**2,700**	11–21	2.6	0.6	

(continued)

Table 1 (continued)

Compounds	Group	Class	Chemical formula	Molecular weight [g mol^{-1}]	Log K_{OW}[a]	Log K_{OC} [mL g^{-1}][a]	Water solubility (**20–21°C**) (*24–25°C*) [mg/L][a]	Persistence in soil – DT_{50} [days][a,b]	GUS	Lowest PNEC in fresh water [μg L^{-1}][c]	EU directives/ watch lists[d]
Desethyl-terbuthylazine			$C_7H_{12}ClN5$	201.7	1.94	2.1	**327**	29	2.8	0.2	
Desmethyl-fluometuron			$C_9H_9F_3N_2O$	218.2		2	304[f]	304	5.0		
Hydroxy atrazine			$C_8H_{15}N_5O$	197.2	1.4	2.9	5.9[f]	32–188	2.2	10	
Metolachlor-ESA			$C_{15}H_{23}NO_5S$	329.4		2.3		235–400	4.2	8.6	

[a] Retrieved from the PubChem (https://pubchem.ncbi.nlm.nih.gov/) and ChemSpider (http://www.chemspider.com/) databases

[b] DT_{50} corresponds to the time for disappearance of half the chemical

[c] Retrieved from the NORMAN database, [16, 17]

[d] 2013/39 refers to Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013 [8]; 2015/495, 2018/840 and 2020/1161 refer to Commission Implementing Regulations (EU) of the Council 2015/495 of 20 March 2015 [9], 2018/840 of 31 May 2018 [10] and 2020/1161 of 3 November 2020 [11]

[e] Clothianidin may be also found in the environment as a transformation product of thiamethoxam

[f] Not available the reference temperature

[g] These are the transformation products of glyphosate, atrazine, atrazine, terbuthylazine, fluometuron, atrazine and metolachlor, respectively

their chemical formula and main physical and chemical properties (molecular weight MW; logarithm of the octanol/water partition coefficient Log K_{ow}; logarithm of the organic carbon-water partition coefficient Log K_{oc}; water solubility; and persistence in soil) and the corresponding PNEC. Compiled pesticides have been classified into groups according to the specific target organism (herbicides, fungicides and insecticides, as reported in the second column) and into classes according to their chemical families (third column).

Herbicides are used for the control of weeds and unwanted plants. These can be formulated to be toxic to specific weeds or weed categories (*selective* herbicides, such as diuron or linuron) or to kill any plants they are applied to (*non-selective* herbicides, as in the case of glyphosate). Herbicides may be applied in different periods during the year. They may be spread (1) to prepare and clean the soil from harmful plants before sowing (*pre-plant* application); (2) after the crop seeds are planted, but before the crop and weeds have emerged from the soil (*pre-emergence* application); and (3) after the crop has emerged (*post-emergence* application) [18]. Sometimes, some herbicides (among them glyphosate) may even be used for crop desiccation to increase harvest yield, and thus are applied at the end of the growing season [19].

The second group of commonly adopted pesticides includes fungicides, which are designed to disturb the energy supply in parasitic fungi and inhibit spore germination [20]. In an agricultural context, fungicides are commonly applied to protect the plants from fungi during their growth and foliation (*post-emergence*) [21]. Other application timings are rarely adopted (e.g. greenhouses).

The third group involves insecticides (Table 1) which are employed for the control of insects and their eggs. The method of action consists of an interaction of the nervous system of their target organisms [22]. One of the most commonly used classes of insecticides is that of neonicotinoids (Table 1). These substances are known for their ubiquity in the environment, due to both their different ways of application and their physicochemical properties which make them particularly prone to be transported in and by water flows [23]. Insecticides are typically used as *post-emergence* pesticides, but they may be applied even before the growing season by seed coating. This practice is being increasingly used as it provides a better protection of the seeds and enhances crop performance [24].

Overall, the three groups of pesticides are typically applied by hydraulic sprayers on the surface of the leaves (*broadcast or foliar application*) or directly on the soil (*soil application*), but other less common methods may be adopted, such as the abovementioned *seed coating*, or the amendment of the topsoil layer with solid granules containing the active ingredient [25]. The application rate of pesticides strongly varies depending on specific country-related usage and legal requirements, as well as the type of treated crop. As an example, the quantity of pesticide used in Europe on a yearly basis per hectare ranges between 0.6 kg ha^{-1} year^{-1} in Latvia and 8.5 kg ha^{-1} year^{-1} in Belgium, while it may reach the extremely higher value of 60 kg ha^{-1} year^{-1} in South America [1].

As shown in Fig. 1, once applied on soil via conventional spreading or seed coatings, pesticides may undergo different biological, physical and chemical

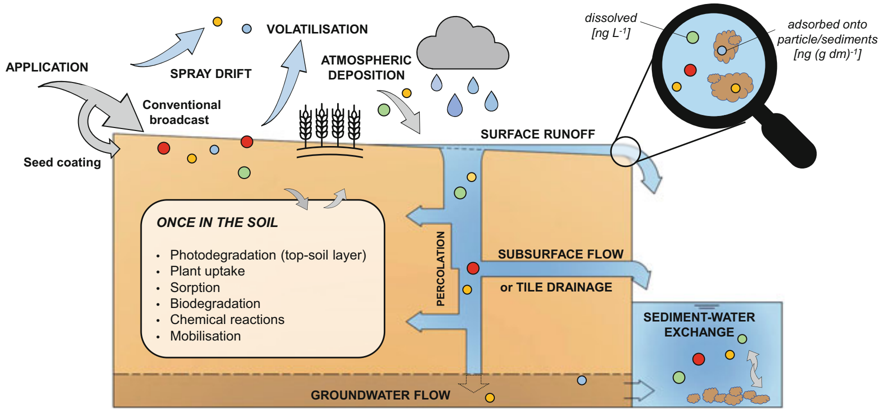


Fig. 1 Potential degradation, transformation and sorption processes and mobilisation pathways of a pesticide after its application on rural soil and routes reaching the surface water or the aquifer

processes and be transported along different pathways. If they are applied via foliar spray, a consistent percentage of the initial pesticide amount may remain in the air and be transported off-site by the wind (spray drift), affecting air quality. Pesticides may reach the atmosphere with the volatilization of water present in the soil [1]. In this context, the application techniques, meteorological conditions and physico-chemical properties of the compound (in particular, the chemical vapour pressure establishing its mass transfer from the liquid to the vapour phase) strongly influence this phenomenon and its consequent off-target contamination [26]. In any case, the fraction of applied mass diffused off-site by spray drift is difficult to assess and only around 2–30% of the total applied amount can be indirectly estimated [27].

In the soil, pesticides may be adsorbed onto the soil particles, undergo biodegradation and chemical reactions, or be uptaken by plants (Fig. 1). The fate of chemical compounds in such a complex system depends on their physicochemical properties and the characteristics of the soil, such as its texture, carbon content, cation exchange capacity, pH and so forth [28]. As a consequence of these concurrent transformation or sorption processes, only a limited fraction of the applied pesticides remains available to be mobilised in the water phase. When an intense rainfall event occurs, water on the topsoil layer tends to percolate, and if the rain event continues, the soil may reach its saturation. The water then starts flowing over the soil surface, generating the so-called surface runoff, which may be considered as a mixture of both water and soil sediments. In this case, pesticides may be transported in the dissolved and adsorbed phases, and their concentrations are expressed in terms of ng L^{-1} and ng g^{-1} dry matter (dm), respectively. If the soil does not become saturated, residues of pesticides in the percolation water flow may be intercepted by tile drains or subsurface flow, or reach the groundwater (Fig. 1).

Finally, part of the pesticides adsorbed on the soil particles transported in these water flows may be moved in the dissolved phase through sediment-water exchange (Fig. 1).

3 Occurrence of a Selection of Pesticides in Surface Runoff

A snapshot of the observed pesticide concentrations in the dissolved and adsorbed phases of agricultural surface runoff is provided in Fig. 2. All the data reported belong to studies published within the last 10 years. The pesticide concentrations were monitored in runoff from both field and simulated rainfall experiments in which pesticides are applied, at a commonly used dosage, with broadcast and foliar spraying or via seed coatings (for some neonicotinoid insecticides). When clear details were provided, the concentrations referring to the first rainfall events monitored after the application were represented as red dots, in order to highlight the importance of the *first-flush* effect in terms of higher environmental impact (due to generally higher concentrations, except for a few cases). Data are provided for the compounds reported in Table 1, which mainly includes current-use pesticides, some historic-use pesticides (e.g. atrazine and permethrin) and some transformation products (e.g. aminomethylphosphonic acid (AMPA) from glyphosate).

Dissolved concentrations of pesticides in runoff (Fig. 2a) vary from 4 ng L^{-1} (for the neonicotinoid insecticide thiamethoxam) to 1,725 μg $\mathbf{L^{-1}}$ (for the chloroacetanilide herbicide S-metolachlor). It emerges that some compounds (namely, clothianidin, dimethomorph, fluopicolide, glyphosate and its transformation product AMPA, imidacloprid, iprovalicarb and S-metolachlor) were most frequently investigated, and a larger number of data are available (35–66 values), while others present a lower amount of data. Focusing on the compounds for which more than 20 data were collected, five of them (namely, clothianidin, fluometuron, glyphosate, S-metolachlor and tebuconazole) exhibit a high range of variability (five orders of magnitude each), while the others exhibit a smaller range (3–4 orders of magnitude).

Different results were found for pesticide concentrations in the sediments transported in runoff (Fig. 2b). Here, the most studied compound (namely clothianidin and imidacloprid, with 46 collected values for each substance) shows a limited range of variability (around 2 orders of magnitude). However, only a few recent studies provided a sufficient number of values, resulting in a lack of data (e.g. a single datum is reported in Fig. 2b regarding deethylatrazine, the transformation product of atrazine, and tebuconazole, the triazole fungicide). Unfortunately, a significant gap in knowledge still exists in differentiating the pesticide load distribution between dissolved and particulate-bound phases [41]. Further research in this respect may contribute to a more realistic environmental risk assessment of non-point contamination sources as well as the development of accurate toxicity benchmarks [45].

Finally, a rapid glance at Fig. 2 shows that most of the reported peaks of concentration were observed in the first hours/days of the monitoring period (red dots). This is attributable to the well-known first-flush effect. The importance of this *phenomenon* affecting the occurrence of pesticides in surface runoff has been studied for many years (e.g. Wauchope [46]), and the investigation of the main parameters

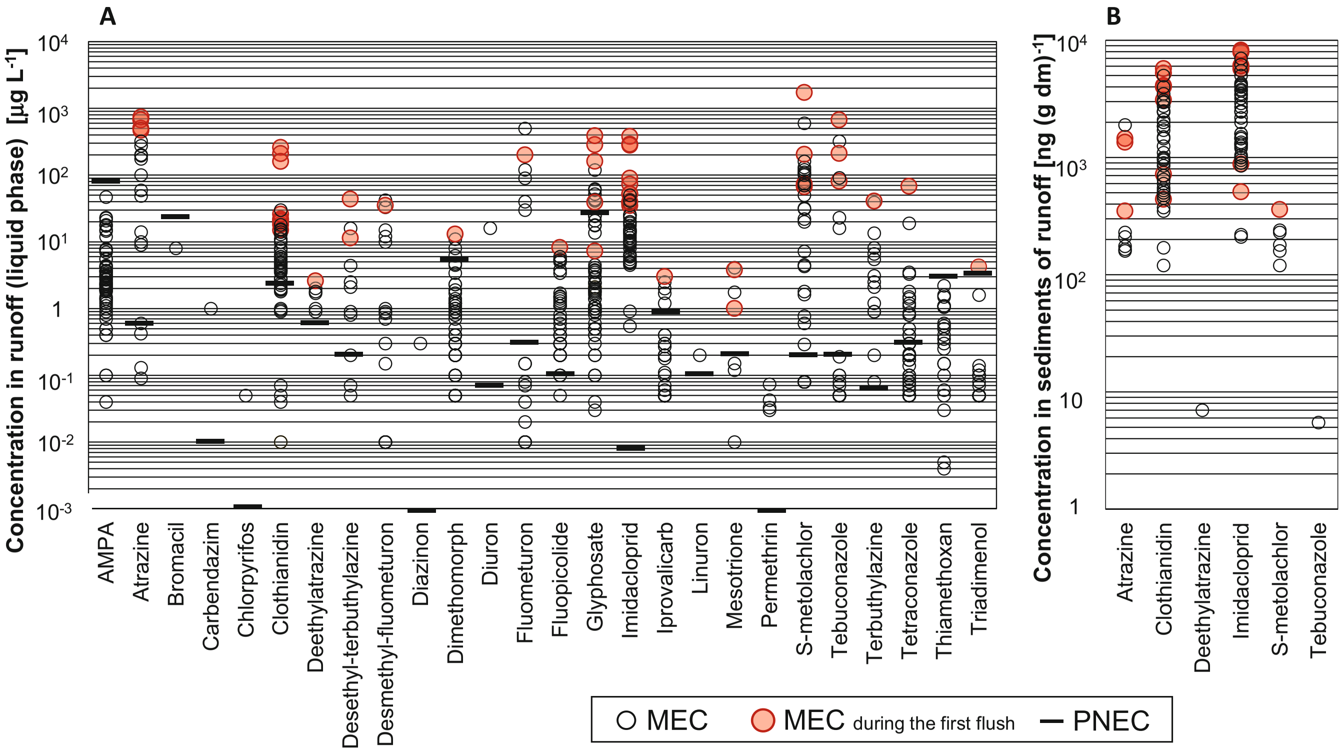


Fig. 2 Measured concentrations (dots) of pesticides in surface runoff: in water (**a**) and in sediment (**b**) and the lowest PNEC for the selected substances (black dashes). Concentrations measured at the beginning of the surface runoff generation, *first-flush concentrations*, are shown with red dots. Data from: [26, 29–43] for water runoff, and [29, 35, 41–44] for sediment runoff

involved in the process is crucial to develop proper agricultural practices that are able to prevent pesticide from transporting into surface water bodies [35].

Figure 2 also reports the lowest PNEC (among the three trophic levels: algae, *Daphnia magna* and fish) for each of the pesticides in the liquid phase of surface runoff. According to the literature [47], if the MEC/PNEC ratio (known as the risk quotient, RQ) is ≥ 1, a high risk is posed for the environment. If RQ <0.1, the risk is low. If RQ is between the two thresholds, the risk is medium. On the basis of the collected data, it emerges that MECs are always lower than the corresponding PNEC, only for AMPA, bromacil, thiamethoxam and triadimenol. For eight substances (namely, carbendazim, chlorpyrifos, deethylatrazine, diazinon, diuron, imidacloprid, linuron, permethrin and terbuthylazine) MECs are always higher than PNEC ($RQ > 1$), and for 12 compounds the PNEC is included in the variability ranges of observed concentrations. A dilution factor up to 10^4 is necessary to guarantee that the concentration in the surface water body, after the introduction of the surface runoff, becomes lower than the PNEC, resulting in a low-medium risk scenario.

On the basis of a mass balance, only a small part of the applied pesticide is generally remobilised and transported by surface runoff. For instance, in a dedicated experiment conducted by Yadav and Watanabe, 2018, it was found that approximately 0.5–2% and 2–6% of the total mass of applied pesticides was moved into water and sediment runoff, respectively. These percentages may differ depending on the affinity of a compound to remain sequestered in the soil, which is thus strictly correlated to the physicochemical properties of the compound (namely, K_{OC}, K_{OW}, water solubility). In this context, Calderon et al. [48] observed in a field experiment that around 0.5% and 0.4% of the applied terbuthylazine (a triazine herbicide with relatively low K_{OC} and thus low affinity to remain in the soil) was moved in runoff water and runoff sediment, respectively, whereas focusing on oxyfluorfen (a diphenyl ether herbicide with high K_{OC}), around 0.03% and 38% of the applied mass was transported in the dissolved and adsorbed phase, respectively.

4 Influence of the Different Parameters on the Fate and Transport of Pesticides

The fate and transport of pesticides in the soil system is governed by various *phenomena* and are affected by different parameters mainly related to the physicochemical properties of the compound, rainfall intensity and pattern, soil characteristics and the presence of buffers or other vegetative filters which may slow down the mobilisation processes.

4.1 Compound Physicochemical Properties

Various behaviours are expected for pesticides once applied onto soil due to their different physicochemical properties. In this regard, it was demonstrated that water solubility, K_{OW} and K_{OC} strongly affect the fate of pesticides in the soil environment. During a rainfall event, compounds which exhibit high water solubility and/or a low K_{OW} (e.g. the neonicotinoid insecticides imidacloprid and clothianidin, or the herbicide glyphosate and its transformation product AMPA, Table 1) are more likely to be mobilised in the water phase, while those with a high K_{OC} (e.g. the insecticides chlorpyrifos and permethrin) are expected to be sequestered in the topsoil layer and to be transported with sediment runoff [49]. In this context, the water solubility and K_{OC} have been used for a long time to classify the mobility of a compound in soil, and dedicated classification schemes have been proposed for this purpose. Examples of this include the solubility and mobility classification criteria provided by FAO and recommended for use by the US EPA [50, 51] reported in Tables 2 and 3.

As a consequence, chemicals with high K_{OC} require more time to be mobilised, or more intense and prolonged rainfall events which trigger sediment transport, which also depends on soil erodibility [32]. Furthermore, it is expected that the concentration of hardly mobile pesticides in water runoff is negligible compared to that in sediment runoff, as demonstrated in the dedicated experiments of Yadav and Watanabe [43].

On the contrary, pesticides with high water solubility are more prone to leaching through preferential flows or to being transported in the first water pulse. As a result, the concentration of soluble compounds in runoff water may follow a highly variable pattern over time, with peaks coinciding with the first hours of rainfall (first-flush

Table 2 Classification of pesticide solubility in water provided by FAO [51]

Water solubility at 20°C (mg L^{-1})	Classification
<0.1	Not soluble
[0.1–1[[a]	Slightly soluble
[1–10[	Moderately soluble
[10–100[	Readily soluble
≥100	Highly soluble

[a] Brackets are used in order to highlight if the limits are included or not. If the lower limit is included, the left bracket is "[", if it is excluded the left bracket is "]", resulting in [0.1–1[

Table 3 Classification of pesticide mobility in soil provided by FAO [51]

Log K_{OC}	Classification
<1	Highly mobile
[1–2[	Mobile
[2–3[	Moderately mobile
[3–4[	Slightly mobile
[4–5[	Hardly mobile
≥5	Immobile

Table 4 Classification of degradability in soil provided by FAO [51]

DT_{50} in soil (days)	Classification
<20	Readily degradable
[20–60[	Fairly degradable
[60–180[	Slightly degradable
≥180	Very slightly degradable

effect) and a drastic decrease after that [35]. Therefore, in view of correctly estimating their transport via surface runoff, it is crucial to properly organise the sampling campaign in order to pinpoint their occurrence and the corresponding variability range of the concentrations [52].

Another important parameter influencing the fate of a pesticide in soil is the time for disappearance of half the chemical (DT_{50}), which is a measure of the amount of time needed for the transformation of 50% of the parent compound considered in a specific environment (e.g. soil, water). A weakly degradable pesticide is likely to be found in its parent form in soil and runoff for prolonged periods (e.g. weeks, months), with consequent risks for the environment. The disappearance time considers both transformations due to biological processes (biodegradation) and physicochemical (or abiotic) processes (e.g. photolysis, hydrolysis, etc.), providing a quick estimation of the persistence of a compound. A classification of the degradability of pesticides in soil is provided by FAO and reported herein in Table 4 [51]. For the selected pesticides, the DT_{50} values are reported in Table 1.

It is interesting to note that pesticides with high water solubility (and thus expected to be mainly transported with the first water pulse) may also be found in consistent concentrations in sediment due to their higher persistence in soil compared to water. This is the case of the neonicotinoids imidacloprid and clothianidin, which, in a simulated rainfall runoff study conducted by Niu et al. [35], were found in both the adsorbed and dissolved phase, despite their pronounced water affinity. The authors suggested that this may be due to the fact that these compounds degrade much more slowly in soil sediments (Table 1) than in water, in which they are easily susceptible to photolysis.

Finally, the Groundwater Ubiquity Score (GUS) index has been defined in order to predict the potential leachability of a compound into groundwater [53]. It depends on TD_{50} and K_{oc} and is given by Eq. 1:

$$\mathrm{GUS} = \log_{10}(\mathrm{TD}_{50})\, x\, [4 - \log_{10}(K_{oc})] \tag{1}$$

A classification of the leachability of a compound based on this index is provided in Table 5. Table 1 reports the evaluated GUS index for the selected compounds. In cases where ranges of Log K_{OC} and DT_{50} were available, GUS was evaluated assuming the average value of K_{OC} and DT_{50}.

An analysis of the most detected pesticides in the groundwater in the Po Valley (Sect. 5) shows that their GUS values are always >2, corresponding to moderate to high mobility, in accordance with Table 5.

Table 5 Classification of mobility in soil towards groundwater

GUS index	Classification
<0	Extremely low
[0–1.8[	Low
[1.8–2.8[	Moderate
≥2.8	High

4.2 Rainfall Intensity and Pattern

The transport of pesticides through surface runoff may consistently vary during the seasons depending on the weather conditions. Pesticides applied in spring and summer may remain sequestered in the soil matrix for long periods, and then be released into the ditches in autumn or winter, after sufficiently intense rainfall events occur [54]. As mentioned above, this *phenomenon* takes place especially for those compounds which are more prone to be bound to soil particles. An extreme example was provided by Sandin et al. [55] which detected residues of terbuthylazine, atrazine and their transformation products in land runoff even if they had not been applied for more than 10 years, as they were banned in Sweden. The authors remarked that illegal use of such substances is highly unlikely for different reasons, concluding that the detected pesticides may have been stored in the subsoil for a considerable time before being remobilised in surface runoff and subsurface flow.

A different behaviour may be observed for compounds that exhibit low sorptivity. Pesticides that are likely to be intercepted by the first water pulse generally exhibit a clear pattern of decreasing concentration over time. During a 10-year monitoring campaign of surface runoff events, Potter et al. [38] observed that every year the highest losses of pesticides in the dissolved phase were observed within the two-week application period, which has been classified as the "critical period" by the well-known study by Wauchope [46]. The so-called *first-flush effect* is commonly observed in many studies, among them Caron et al. [30]; Milan et al. [34]; Niu et al. [35] carried out in both real weather and simulated rainfall conditions, and especially for hydrophilic pesticides. Similar patterns were noted for their transformation products but, as expected, their peak concentration is commonly measured in the second and third rain event or, in any case, after a window of time long enough for the degradation of the corresponding parent compounds [30].

For these reasons, the number of applications also plays an important role in the behaviour of pesticides in soil. Considering an equal application rate, a pesticide applied more times during the growing season (such as in the case of the fungicide tebuconazole, which may even be sprayed 3–5 times per season at fortnightly intervals) has a greater possibility of being mobilised in surface runoff than a single-application pesticide (such as the herbicide S-metolachlor), which has a better chance of being adsorbed in soil particles and then degrading [39].

Finally, rainfall intensity and volume also considerably affect the transport of pesticides in soil. Even in this case, pesticides with different water-soil affinity may exhibit different behaviours: high intensity rainfall events may result in soil erosion and, consecutively, in sediment runoff, in which it is expected to find compounds with high K_{OC}. On the other hand, low intensity rainfall events, but of long-duration, seem to enhance the mixing of the pesticides in the topsoil layer, with consequent remobilisation in the water phase of those with higher water affinity [40].

4.3 Soil Characteristics

In monitoring surface runoff of pesticides, many studies (among them Dunn et al. [56]; Stehle et al. [57]; Wang et al. [42]) observed that soil slope often plays a key role in influencing the *phenomenon*. It is well known that a steep slope (>5–10%) makes the soil easily erodible, especially in bare land conditions, entailing sediment runoff of compounds with high soil affinity [48]. However, Niu et al. [35] also observed that the transport in sediment runoff from a steep slope of imidacloprid and clothianidin was relevant even if the two neonicotinoid insecticides exhibit high water solubility and low K_{OW} (Table 1), suggesting that a high slope may also entail the mobilisation of the low fraction of those pesticides bound to soil particles. This observation was corroborated by the fact that the transport of imidacloprid and clothianidin was strongly reduced in plots covered by weeds or biological crusts, in which erosion is more difficult to occur.

In gentler slopes, other parameters also seem to significantly influence the mobilisation of pesticides in runoff. First of all, the vertical water flows are consistently affected by soil texture. While sandy soil generally acts as a soil filter in which pesticides may be trapped and start degrading, while clayey soil is more likely to develop cracks and macropores that results in vertical preferential flows [49]. This may lead to a lower pesticide transport in surface runoff, but also to a higher risk of groundwater contamination, or pesticide occurrence in tile drainage, if they are present.

Furthermore, the mobility of pesticides in soil is influenced by the sorption/desorption *phenomena*. Within the soil the sorption is mainly governed by soil organic carbon (OC) content and, to a smaller extent, by dissolved OC and temperature [58]. In particular, adsorption seems to increase with temperature and soil OC content, but dissolved OC may compete with pesticides for the binding sites of soil OC [59]. Here, not all the adsorbed mass is expected to be remobilised with desorption. This last process usually does not proceed reversibly, resulting in desorption hysteresis, and therefore delaying the leaching of chemicals [60].

Another property controlling pesticides adsorption/desorption process is soil pH. On the one hand, adsorption seems to increase as soil pH decreases (especially for ionisable compounds) while, on the other, higher soil pH may enhance degradation [58]. In any case, many processes may occur within the soil matrix, resulting in the difficulty of analysing the parameters that mostly influence the transport of pesticides, and the interactions between the various *phenomena*.

5 Effects of Land Runoff on the Water Compartments: Analysis of Some Case Studies

As remarked above, once pesticides are applied on the soil, they are subjected to different assimilation/adsorption/degradation/transformation processes and also to mobilisation within the soil. They may also reach the water compartments (groundwater and surface water) transported by the flow present in the soil or enter due to rain events or irrigation. As reported in Table 1, their persistence in the soil, expressed in terms of DT_{50} varies from a few days (in the case of diazinon and chlorpyrifos) to more than 1 year (for instance, for tetraconazole, fluopicolide and clothianidin). The DT_{50} value mainly depends on soil type, pH, temperature and irradiation. Intense rainfall events favour leaching of chemicals present in the soil, solid transport (due to soil erosion) towards surface water bodies and, at the same time, they promote the movement of chemicals towards groundwater. These phenomena have been deeply discussed in [61] with regard to micro-contaminants in runoff in the case of sludge-amended soil.

The occurrence of pesticides in water compartments is analysed herein with regard to Italy and some details are provided for the largest agricultural region in Italy, the Po Valley (Fig. 3). This is a rural area covering 46,000 km^2 that has developed in the north of the country along the Po River (650 km long) and its numerous tributaries. Annual precipitations range between 700 and 1,200 mm and are equally distributed throughout the year, with maximum values in autumn and spring. The area drains main agricultural and industrial zones. Many different types of crops are present: cereals, soybean, rice, fruit trees and vegetables, requiring a large spectrum of pesticides. According to the last report by ISPRA, the Italian Institute for Environmental Protection and Research, [62], it emerges that between 2017 and 2018, the national annual amount of pesticides sold was on average 4.3 kg ha^{-1} $year^{-1}$, with a minimum of 0.3 kg ha^{-1} $year^{-1}$ in Aosta Valley, a mountainous region, and a maximum of 12.4 kg ha^{-1} $year^{-1}$ in Veneto (where agriculture is the most important economic sector). The national average is lower than the corresponding value referring to 2015–2016, which was 4.6 kg ha^{-1} $year^{-1}$ [63]. It was also found that in 2017–2018, in the regions located in the Po Valley, this value is higher than the national average, varying between 4.5 kg ha^{-1} $year^{-1}$ and 12.4 kg ha^{-1} $year^{-1}$.

Monitoring campaigns are regularly planned for more than 400 pesticides over the year for both surface water bodies (around 2,000 sampling points) and the groundwater network (around 3,000 points). Based on these investigations, it was found that, in 2018, pesticides were detected in 77% of the monitoring points in surface water and in 54% of the water samples, and in 35% of the groundwater monitoring points and in 31% of the water samples.

The most detected substances in surface water were AMPA (frequency detection equal to 65%), glyphosate (42%), metolachlor-ESA (30%), imidacloprid (20%) and S-metolachlor (19%), whereas in groundwater they were atrazine desethyl desisopropyl (21%), flonicamid (19.5%), metolachlor-ESA (18%), desethyl-

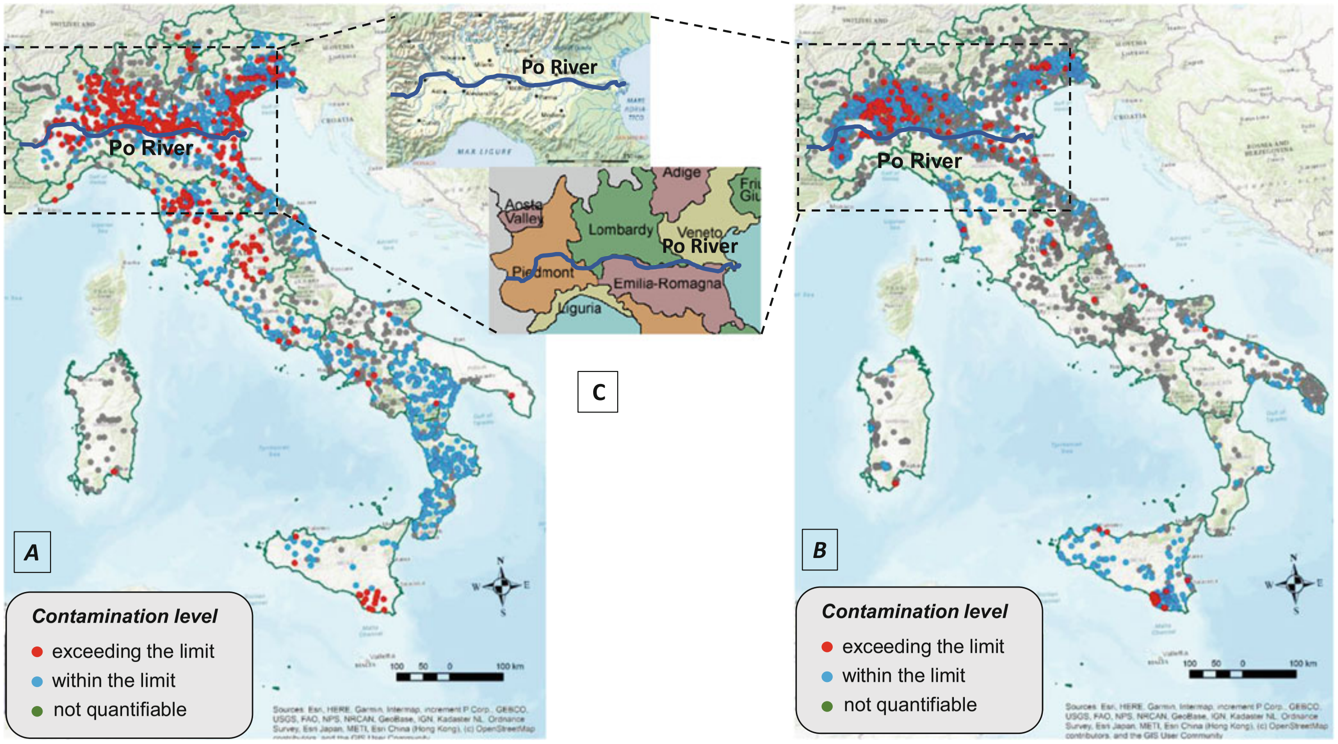


Fig. 3 Contamination level due to residues of pesticides in surface water (**a**) and in groundwater (**b**) in Italy. Physical and political maps of the Po Valley (**c**) (Adapted from [62]). Sources: Esri, HERE, Garmin, Intermap, increment P Corp., GEBCO, USGS, FAO, NPS, NRCAN, GeoBase, IGN, Kadaster NL, Ordnance Survey, Esri Japan, METI, Esri China, (Hong Kong), (c) OpenStreetMap contributors, and the GIS User Community

terbuthylazine (15%), hydroxyatrazine (14%), carbendazim (11%) and deethylatrazine (11%).

It was also found that the occurrence of the mixtures of pesticides is higher than in the past years: four substances were found on average, but in some cases, 56 pesticides were present in water samples.

An analysis of the contamination level due to residues of pesticides is carried out with regard to the limits (maximum admissible concentrations) in surface water defined by the Italian decree (D. Lgs 172/2015 [64]) which transposes the European Directives (Directives 2008/105/EC [65] and 2013/39/EU [8]). For compounds (included their metabolites) not included in the Italian decree, the value of 0.1 μg L^{-1} is set for the maximum concentration of each of them and 1 μg L^{-1} for their sum. If the surface water is withdrawn for potable needs, this limit reduces to 0.5 μg L^{-1}.

As to groundwater, the limits for pesticides and their transformation products are defined by D. Lgs 30/2009 [66] which transposes Directive 2006/118/EC [67] on the protection of groundwater from pollution. The limits correspond to those set for drinking water: 0.1 μg L^{-1} for the single substance and 0.5 μg L^{-1} for the sum of different substances.

Figure 3a, b shows the results related to the years 2017 and 2018. It is evident that the monitoring networks are more developed in the north than in central and southern Italy. The collected values of concentrations of pesticides exceeding the limits are generally in the north, most of them in the Po Valley due to the extensive application of different types of pesticides for the different crops. In surface water, at a national scale, the exceeding values occur for glyphosate and its metabolite AMPA, respectively, 21.7% and 54.3% of the monitored sites followed by metolachlor (3.3%) and its metabolite metolachlor-ESA (5.3%), whereas, in groundwater, the fungicide carbendazim presents the highest number of exceedance (3%), followed by glyphosate (2%) and AMPA (1.6%). Since 2016, the use of glyphosate in Italy has been prohibited in public areas as well as in vulnerable areas and before harvest. Regarding the neonicotinoids clothianidin, thiamethoxam and imidacloprid, since 2013, the tanning of seeds has been prohibited as well as the treatment of cultivations which attract bees.

The fungicide carbendazim was banned in 2014. It is still present in water (mainly groundwater) due to its persistence (DT_{50} up to 360 days).

Based on the collected data, 98% of the pesticides leached via runoff is due to a few intense rainfall events with a return period of 25–27 years, while 3–4 runoff events of modest intensity are expected during the irrigation season (from May to October) [68]. Due to increasingly frequent extreme rainfall events, the loss of pesticides through land runoff seems to represent an uncontrollable diffuse source threat for the surface water network. This has led to the adoption of mitigation measures to reduce the potential negative effects. As will be discussed in more detail later on, vegetated agricultural drainage ditches, designed for drainage purposes, favour the development of living organisms and plant species and, at the same time, act as an equalisation corridor in the case of runoff, thus protecting the watercourses. In this context, it was found that for herbicides with K_{oc} between 110 L kg^{-1} and

400 L kg^{-1}, a runoff of 1 mm from 5 ha is mitigated by 99% in a 100 m long and 1 m wide vegetated ditch. The main dissipation pathways are adsorption on sediments and bio- and photo-degradation.

The environmental risk posed by residues of pesticides in surface water bodies was assessed in the Jumilla region, a 25,000 ha-wine production area in the southeast of Spain. This area is characterised by an irregular rainfall pattern with long periods of drought. The average annual rainfall is around 300 mm. Rain events are concentrated in spring and autumn and are generally torrential. As a consequence, water is not absorbed by the soil, but it runs off in torrents and dried-up river beds [17]. The risk quotient approach was adopted, based on the evaluation of the ratio between MEC in the water and PNEC for algae, *Daphnia magna* and fish. They found that based on their monitoring campaign, the compounds with the highest risk were the herbicides pendimethalin with a high risk ($RQ \geq 1$) for the three aquatic organisms, and diflufenican posing a high risk for algae and fish, and the insecticide chlorpyrifos with a high risk for *Daphnia magna* and fish.

In the vulnerable area of the Ebro Delta, Catalonia, Čelić et al. [69] found that a high risk for algae and fish is posed by the herbicides terbuthylazine, desethyl-terbuthylazine and terbutryn, the fungicides azoxystrobin, tebuconazole and prochloraz, and the insecticide tebufenozide.

6 Best Practices to Reduce Pesticide Transport

Bearing in mind the factors that influence the transport of pesticides mentioned above, in recent years, agronomists and researchers have tried to develop easy and cost-effective systems to reduce arable land surface runoff.

In this context, pesticide transport may be reduced directly in the field (at the source) by means of irrigation with polyacrylamide (PAM), a long-chain polymer used for erosion control, or by adopting adequate tillage practices [37]. An example of the latter is the strip tillage, a commonly used soil conservation-tillage practice, which consists of disturbing only the portion (strip) of arable land in which the seeds are going to be sown. In dedicated experiments in which the transport of pesticides was compared in conventionally and strip tilled fields, Potter et al. [38] found that the second practice led to around a 75% reduction in pesticide mass in water runoff due to the higher infiltration capacity and vegetation obstacle promoted by the strips. Similar results were found in the investigation by Niu et al. [35] in which the sediment runoff of pesticides was significantly lower in fields with biological crust or taller weeds compared to that in bare lands. Furthermore, Potter et al. [37] observed that strip tillage also led to an attenuation of the first-flush effect, probably due to both the erosion control of the vegetation and the reduction in the kinetic energy of raindrops.

The transport of pesticides in surface runoff may also be reduced after its formation in the field (at the end-point), by collecting the water and sediment runoff in dedicated retention basins, and by intercepting the flow in ditches in which vegetation or other barriers (e.g. compost heaps) are set [68], or even in vegetated buffer strips (VBSs) [37]. The latter have been thoroughly studied and are commonly adopted as they represent a cost-effective solution for farmers. The mechanism of pesticide transport attenuation with VBSs belongs to both sediment trapping and water infiltration, for compounds that tend to be adsorbed in sediment or dissolved in water, respectively. For this reason, with all the other factors being held constant (rainfall intensity and pattern, soil characteristics, pesticide physicochemical properties and so forth), the reduction of pesticide concentration in surface runoff is mainly affected by the buffer width and type of plant grown in the strip [49]. Many investigations (among them Carretta et al. [31]; Milan et al. [34]; Otto et al. [36]; Wang et al. [42]) reported that buffer strips 1–6 m wide and planted with different species of local common weeds led to a 55–95% reduction in a broad spectrum of compounds, and their transformation products, with different characteristics. Despite this, the results of Caron et al. [30] drew attention to the potential risk of enhancement of vertical transport (e.g. subsurface flow, or tile drainage when tiles are installed) of pesticides due to the increased infiltration in the root zone in plots in which vegetation is planted. In any case, better performance and the related lower environmental risk can be achieved by integrating two or more of the best practices mentioned above. Such combinations of VBSs, tilling methods and retention basins, which are commonly referred to as integrated vegetative treatment systems, may act as a barrier for both lateral (e.g. surface runoff) and vertical (e.g. tile drainage) flows. An example of this was reported by Phillips et al. [37] which combined irrigation with PAM with subsequent conveyance of the surface runoff in grass-lined ditches with compost sleeves (or also biochar sleeves), which obtained a 99% reduction in the mass transport of imidacloprid and permethrin in runoff.

7 Final Remarks and Needs for Future Research

The overview here presented highlights that the occurrence of pesticides in surface runoff may vary in the range of ng L^{-1} to μg L^{-1} in the liquid phase and ng (g dm)$^{-1}$ to μg (g dm)$^{-1}$ in the transported sediments. It also emerges that data referring to the latter are still lacking for many compounds. The presence of pesticides in surface runoff is strongly influenced by their physical-chemical properties, soil characteristics and rainfall intensity and pattern. Pesticides release in the aquatic environment may have negative (acute or chronic) effects on living organisms, especially in the case of small receiving water bodies in which the dilution is not sufficient to reduce the pesticides concentration below their corresponding PNEC. The adoption of mitigation measures, such as the different types of vegetated treatment systems, may contribute to reducing the environmental risk posed by residues of pesticides in surface runoff.

Research efforts in the near future should involve monitoring investigations referring to current-use pesticides. Proper sampling approaches have to be adopted in order to better assess variations of concentrations in relation to rainfall intensity, pesticide calendar and rate and sediment-water exchange [70]. Promising solutions may include (1) high frequency sampling estimating peak pesticides concentrations and (2) passive sampling techniques providing average concentrations over a long period of time, for a comparison with the corresponding EQS defined by the Water Framework Directive [12]. Attention should also be paid to the occurrence of pesticides in sediments transported by the surface runoff and to the complex phenomena of sorption-desorption and degradation within the soil, especially for currently used pesticides. Finally, ecotoxicological studies are required to assess the acute and toxic effects of mixture of pesticides in water. At the same time studies should also focus on the design of proper vegetated treatment systems in order to mitigate the impacts by means of easy-to-build and cost-effective solutions.

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Pesticide Fate in Soils Under Different Agricultural Management Practices

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Contents

Abstract Agricultural development and the sustainability of agrosystems are two topics of great current interest. The typical model of intensive or conventional agriculture provides highly productive agrosystems, but at an important environmental cost. Therefore, new cropping systems, soil management and/or agricultural practices are being put in place to ensure sustainable agricultural production and reduce the environmental impact, as a challenge facing agriculture both now and in the future. However, the use of pesticides remains necessary even in this new approach to agricultural management, as well as tracking their fate in these systems because it has generally been studied under conventional practices. Some laboratory-scale studies have reported the effects of these practices, but few studies have been conducted under field conditions. Accordingly, this chapter conducts a review of

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current studies including pesticide persistence, dissipation and mobility in soils according to conservation agricultural practices, such as the soil application of organic amendments, conservation tillage systems or crop rotation. The chapter also includes a review of existing models to simulate pesticide behaviour under these management practices. Finally, a summary with research gaps and recommendations is proposed for the future development of modelling under conservation practices as tools for predicting possible long-term soil and/or water pollution.

Keywords Agricultural systems, Contamination, Dissipation, Environmental safety, Field experiments, Mobility, Modelling, Persistence, Pesticide

1 Introduction

Agriculture today seeks a high yield in the shortest possible time. This model is defined as intensive or conventional agriculture and is based on excessive soil tillage and irrigation, and the use of nitrogen, potassium and phosphorus fertilisers and pesticides. This type of agriculture provides highly productive agrosystems, but at an important environmental cost. The negative consequences include soil depletion and its degradation, significant water pollution (nitrate and pesticides), eutrophication (phosphorus and nitrate), air pollution due to pesticide volatilisation and greenhouse gas emissions (CO_2 and N_2O) that contribute to climate change and its effects (i.e., global warming, drought, floods, etc.) [1, 2]. New cropping systems, soil management and/or agricultural practices have been designed, implemented and/or restored in the primary sector in the last decades with a view to resolving or minimising these negative consequences, ensuring the sustainability of agrosystems and decreasing pollution. These practices are commonly referred to as conservation agriculture because their main objective is to address agricultural production and its environmental impact in a sustainable manner [3–5]. These practices include the following: (1) the application of organic amendments to soil, (2) conservation tillage systems and (3) crop rotation (Fig. 1). The restoration and/or implementation of these new agriculture practices has numerous environmental benefits, focused mainly on the preservation of soil fertility and its present and future agronomic value. Accordingly, all these agricultural practices and soil management have important social and agricultural benefits [6, 7].

The use of pesticides, however, continues to be necessary, to a greater or lesser extent, even in conservation agriculture. Farmers consider pesticides to be essential compounds for increasing crop yields by controlling the pests and diseases that threaten our food supply. Some studies estimate losses in most crops of 40% or even higher [8] due either to pests or to the competition between crops and weeds for soil nutrients. There is therefore a need to combine conservation agriculture and the use of pesticides to preserve soil quality and obtain high crop yields. This involves understanding the fate of the pesticides applied to assess and minimise their potential

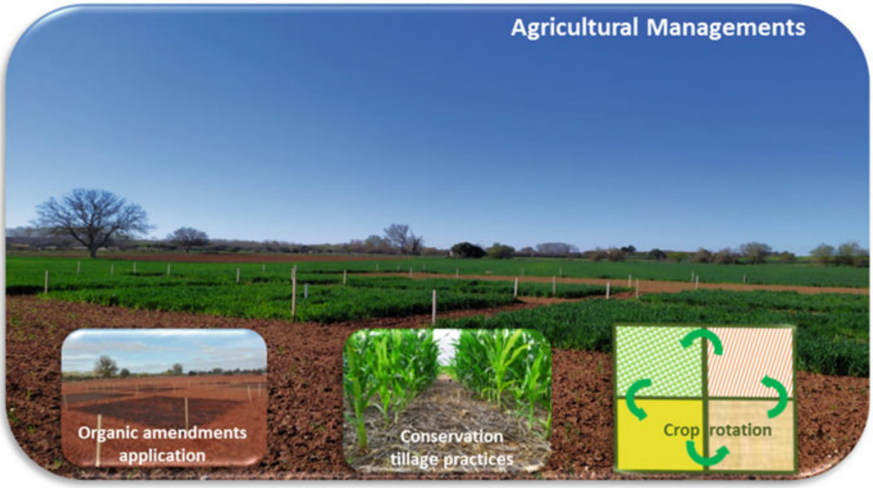

Fig. 1 Different conservation management practices

environmental risk to soil and water quality. This is particularly important when considering the increasing contamination of water sources by pesticides in agricultural areas around the world. In some cases, concentrations higher than the limit established for drinking water by EU legislation (0.1 μg L^{-1}) have been recorded, understandably raising public concern [9–11].

The fate of pesticides in soils is generally studied when applying conventional practices, and only under these practices is their behaviour also evaluated during the registration process for their authorisation and later application [12, 13]. Field experimental data on pesticide dynamics in soils under these new agricultural practices, such as the application of organic amendments, conservation tillage systems or crop rotation, as well as their modelling, are less frequent, and they will be evaluated in this review. Although a few studies have been conducted under field conditions [14–17], the effects of these practices have generally been analysed at laboratory scale. However, data obtained under real conditions are required to design an environmentally safe and effective application, and subsequently model pesticide behaviour in order to predict its persistence, dissipation and/or mobility under these agricultural practices.

This review includes current studies on the persistence, dissipation and mobility of pesticides in soils under field conditions when conventional or new conservation management practices are applied. The main parameters and/or processes reported are identified under these conditions and provide information for modelling. Furthermore, the chapter includes a review of existing models for simulating pesticide behaviour and making recommendations for the future development of these models under conservation practices, as tools for predicting possible long-term groundwater pollution.

2 Use and Fate of Pesticides in Soils

About 3.5 million tonnes of pesticides are currently being applied worldwide, and the figure is expected to increase in the future to ensure the global food supply. The world's population currently stands at over 7.7 billion people and is expected to rise to 9.6 billion by 2050 [18]. Among the wide variety of pesticides used in agriculture, the highest percentages correspond to herbicides (48.5%), followed by fungicides and bactericides (26.6%), and insecticides (18.9%) [19]. The top ten countries using pesticides (Fig. 2) are China, USA, Argentina, Thailand, Brazil, Italy, France, Canada, Japan and India [20].

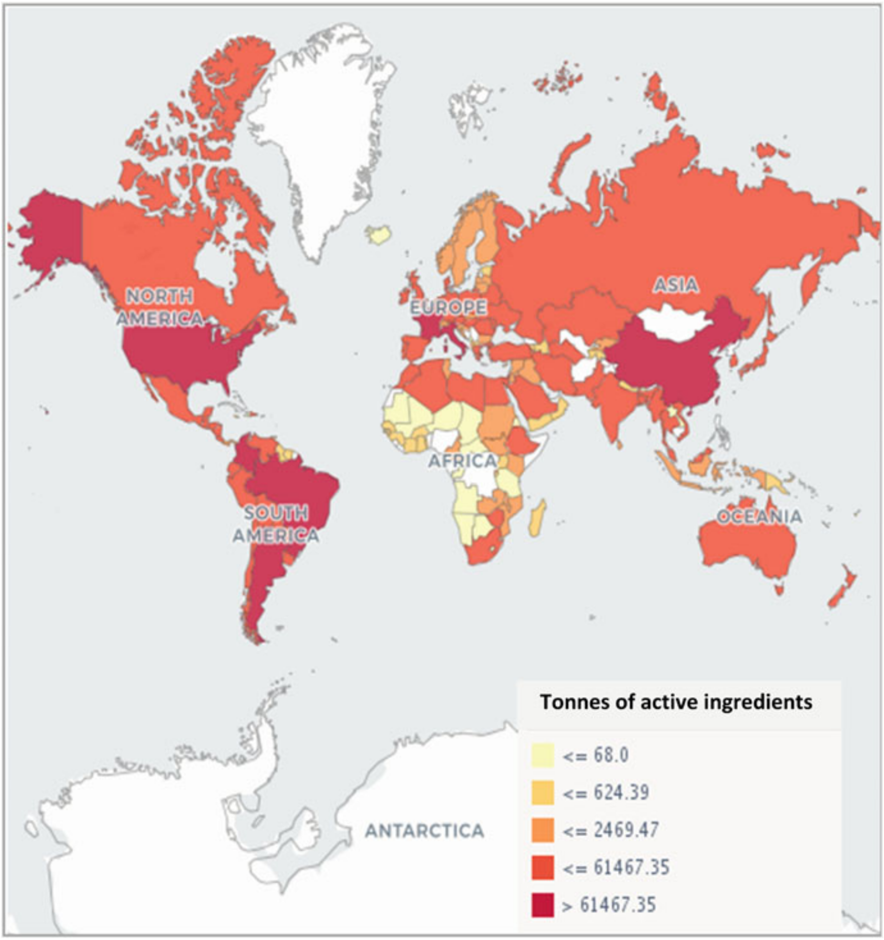

Fig. 2 Average use of pesticides (tonnes of active ingredients) in the world for the period 2000–2016 [20]

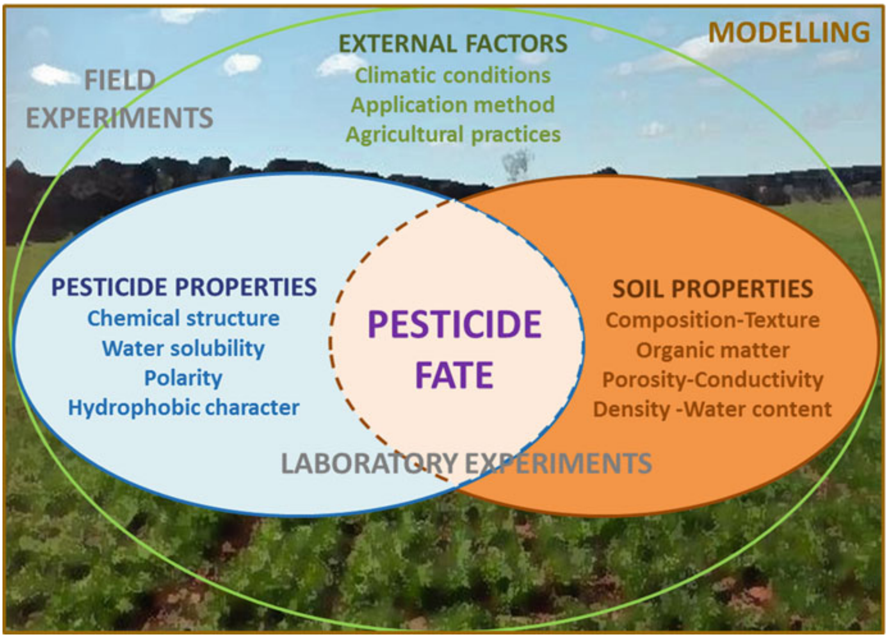

Fig. 3 Factors influencing the dynamics of pesticides in soil

Pesticides applied in the field undergo different processes when they reach the soil: adsorption-desorption, chemical, photochemical and microbiological degradation and/or dissipation, and mobility including leaching, runoff and volatilisation. On the one hand, these processes depend on pesticide properties (chemical structure, water solubility, polarity, hydrophobic character), soil properties (granulometric composition, texture, organic matter (OM), porosity, hydraulic conductivity, density, water content, microbial composition) and on the other, on external factors (temperature, precipitation, wind, radiation, application method, agricultural practices) [21] (Fig. 3).

Pesticides are retained by soil components through different adsorption mechanisms, with soils with higher OM and clay content having a higher potential for pesticide persistence [22]. OM could favour the adsorption of hydrophobic compounds through bonds that reduce their bioavailability for degradation by soil microorganisms, increasing their persistence [23–25]. Pesticide degradation by soil microorganisms is the main dissipation process for many compounds, and it is usually rapid when there is enough moisture in the soil and the temperature is warm. The chemical degradation (chemical hydrolysis) of pesticides could also be affected by soil pH, and it has been reported to explain the degradation of certain herbicides, such as triazines and sulphonylureas [26–28]. Finally, pesticide mobility depends on both adsorption and degradation processes controlling the extent to which this process occurs, so it should not be studied independently [25, 29].

In general, these studies have been conducted in the laboratory under controlled conditions. However, extrapolating laboratory results to the field is of limited value because laboratory conditions are not representative of real conditions. The most frequent experiments simulating field conditions as those carried out with samples collected in the field after different ageing periods [30]. However, field conditions record the interactions of multiple variables and changes in soil structure (mainly clayey soils) due to the effects of the soil moisture cycle [31], or to the soil environment caused by climate change variables [32]. Consequently, pesticides can behave differently in the field [33]. This requires extending these studies to field scale under real conditions, thereby allowing for the consideration of additional factors such as the undisturbed soil structure, weather and irrigation conditions, or the presence of crops modifying pesticide dynamics through plant uptake, or simply controlling water dynamics (Fig. 3). In addition, the modelling of pesticide fate in new agricultural scenarios is required to avoid compromising the sustainability of soil and water resources, while at the same time evaluating its agronomical benefits. There is a significant gap in this research field, as evidenced by the scarce studies reported in the literature, especially regarding the fate models usually applied for pesticide registration purposes [34, 35].

3 Effects of Different Factors Influencing Pesticide Fate Under Conventional Agriculture

Field experiments for evaluating the fate of pesticides in soils under conventional agriculture are generally reported to provide data for the application of models that allow extrapolating the behaviour of pesticides applied in the long term or under variable environmental conditions. Pesticide fate data under conventional agricultural practices are necessary as a reference when new agricultural practices are applied. In fact, pesticide behaviour under conservation agriculture is usually studied in comparison with conventional practices [35–37]. Some environmental and edaphic factors, such as the effect of different irrigation and weather conditions, the timing of application, or changes in soil structure are considered of particular relevance when evaluating pesticide fate under conventional field practices (Table 1). However, these factors' influence may be different when different agricultural managements other than conventional ones are applied.

Gupta et al. [38] have studied the persistence and mobility of the herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) under three different irrigation regimes between field capacity and wilting point to understand the significance of soil water content in pesticide behaviour. They have indicated that the safe dosage of pesticide application is governed by irrigation. No residues have been found in an unsaturated soil zone in Roorkee (India) under three different irrigation treatments due to their degradation by the end of the wheat crop season. However, crop irrigation frequently involves wastewater with variable content in dissolved organic

Table 1 Factors influencing pesticide fate under conventional agriculture practices

Pesticide	Chemical group	Activity	K_{ow}	Water solubility (mg/L)	DT_{50} field (days)	Factor	Reference
2,4-D	Alkylchlorophenoxy	Herbicide	−0.82	24,300	28.8	Irrigation regimes	[38]
Atrazine	Triazine	Herbicide	2.7	35	29	Wastewater irrigation	[39]
Azoxystrobin	Strobilurin	Fungicide	2.5	6.7	180.7	Timing of pesticide application	[40]
Propiconazole	Triazole		3.72	150	35.2		
Fluazifop-P-butyl	Aryloxyphenoxypropionate	Herbicide	4.5	0.93	8.2	Amount of precipitation	[41]
Imidacloprid	Neonicotinoid	Insecticide	0.57	610	174	Simulated rainfall experiments	[42]
Clothianidin		Insecticide	0.905	340	121.2		
Flufenacet	Oxyacetamide	Herbicide	3.5	51	39	Weather conditions	[43]
Diflufenican	Carboxamide		4.2	0.05	64.6		
Pendimethalin	Dinitroaniline		5.4	0.33	100.6		
Flufenacet	Oxyacetamide	Herbicide	3.5	51	39	Weather and soil structure	[44]
Atrazine	Triazine	Herbicide	2.7	35	29	Weather and soil structure	[45]
Quizalofop-p-ethyl	Aryloxyphenoxypropionate	Herbicide	4.61	0.61	1.8	Field dissipation	[46]
Fomesafen	Organochlorine	Herbicide	−1.2	50	86	Field dissipation	[47]

matter (DOM), which could modify the transport of pesticides in soils, as indicated by Peña et al. [48] in a recent review. Salazar-Ledesma et al. [39] have evaluated whether the effect due to wastewater irrigation could increase groundwater pollution by these compounds. They have studied the mobility of atrazine and its metabolites in a maize field in the Mezquital Valley in Central Mexico, where the use of atrazine is still allowed. The mobility of compounds with the first irrigation has been detected, and it is suggested that the application of the herbicide should be performed some days after irrigation to allow greater contact time and enhance adsorption between atrazine and the soil.

The timing of pesticide application is considered a crucial factor for pesticide leaching, and the application of these compounds a few days after irrigation has been proposed to promote their adsorption and degradation by soils and avoid their leaching into deeper layers. Edwards et al. [40] have indicated that the timing of application in relation to the first precipitation event significantly affects the loss of azoxystrobin and propiconazole and the predominant mode of transport for these compounds by agricultural runoff water. Similarly, a long-term study by Vendelboe et al. [41] has shown that the amount of precipitation falling within a week of application of fluazifop-P-butyl is the controlling factor for the leaching of the degradation product (5-(trifluoromethyl)-2(1H)-pyridinone) to drainage and groundwater.

With a view to mitigating the risk of pesticides from runoff, Yadav and Watanabe [42] have evaluated the runoff potential of imidacloprid and clothianidin in an upland field under two simulated rainfall experiments. The results show that the second rainfall experiment prompted a greater transport of insecticides because there was more surface runoff and sediment transport than from the first rainfall experiment, with the insecticides being transported mainly in runoff sediments.

The effect of weather conditions on pesticide fate has been addressed by Willkommen et al. [43], who have evaluated the leaching of flufenacet, diflufenican and pendimethalin in a tile-drained landscape. The authors have indicated that wet weather conditions lead to a tenfold increase in daily drainage loss for all pesticides, and the weather conditions linked to pesticide properties control their transport. In turn, wet and dry weather conditions could also affect the leaching of flufenacet and/or degradation products to shallow groundwater by preferential pathways [44]. A greater risk of preferential flow has been found for this compound during dry weather, as opposed to wet conditions, and consequently low precipitation events tend to produce peak herbicide concentrations in groundwater. In contrast, flufenacet and flufenacet-ESA record the opposite behaviour because the degradation product is continuously detected in shallow groundwater. Under wet conditions, the significance of preferential transport is apparently reduced, and a large fraction of flufenacet is transformed into flufenacet-ESA.

This effect of soil structure on herbicide leaching has also been addressed [31, 45]. Dor et al. [45] have characterised the effects of wetting and drying on soil microstructure, aggregate packing and stability, and the subsequent effect on atrazine mobility in three agricultural soils. The adverse effects of wetting and drying on soil structure affect atrazine mobility because it is trapped within the clay soil aggregates, and disaggregation leads to a 35% increase in pesticide mobility, whereas the stabilisation of sandy clay loam aggregates reduces atrazine leaching by 23%.

Herbicide dissipation for different crops under field conditions has frequently been studied to discover whether it is transferred by runoff water in soils. In this respect, quizalofop-p-ethyl is considered a very low risk herbicide for adjacent water resources due to its low soil persistence [46]. The low persistence of the herbicide fomesafen in the top soil has also been reported, although ≈3% of the compound applied persisted in the subsoil >3 years after application [47].

4 Fate of Pesticides in Soils Following the Application of Organic Amendments

The application of composted organic residues as organic soil amendments is a widespread practice in intensive farming systems designed to increase soil OM content. It seeks to avoid the problems of soil degradation and its associated erosion due to a low OM content [49, 50]. Soil OM plays a fundamental role in the development and functioning of land ecosystems, and its content is considered the main factor of soil fertility because it improves its stability, increasing its porosity and water retention capacity, favouring the exchange of gases and water, as well as the exploratory capacity of plant root systems [51–53]. As a result, the soil is protected against surface runoff and erosion, and OM helps to improve the revegetation of degraded soils [54–56]. Some authors have also reported that this farming practice may be used for carbon sequestration and regulating emissions of carbon dioxide and other greenhouse gases [57, 58]. Among the residues potentially applicable as organic soil amendments are the following: urban (sewage sludge or urban solid wastes), agricultural (crop residues), livestock (manure and slurry) and agro-industrial activities (wine, beer and olive production, and mushroom cultivation) [59–61]. They are applied at different rates, and the increase in soil OM depends on the residues' total organic carbon (OC) content.

Some studies, nevertheless, have reported that the environmental fate of pesticides could be modified when organic residues and these compounds are simultaneously applied to soils with different crops [62]. The application of these organic amendments may alter the physicochemical behaviour of pesticides depending on the characteristics of both pesticides and organic amendment and the dose of amendment applied. Organic amendments increase the soil OC content, and this is the main factor influencing the adsorption/retention process of mainly non-ionic, hydrophobic pesticides by soils with low or very low solubility in water [14, 62, 63]. This increase in adsorption leads to the immobilisation of pesticides, affecting their degradation, persistence or mobility. This could increase their subsequent degradation, decreasing their transport through the soil profile, and consequently reducing groundwater pollution in some cases [64–67]. However, it could also affect the final concentration bioavailable for their absorption by the targeted weeds [68]. The addition of organic soil amendments introduces dissolved organic matter (DOM), which enhances the mobility and transport of these compounds, as it facilitates hydrophobic interactions between pesticides and DOM in the water, increasing the solubilisation and transport of these compounds with the consequent contamination of groundwater [69, 70]. These processes depend on the characteristics of the pesticide, the dose and composition of the applied amendment, or its evolution in the soil after its application [71].

4.1 Effects of Organic Amendments on the Fate of Pesticides in Soil

Organic amendments are applied to soil in different types of crops, and pesticides applied in amended soils are compounds with herbicide, fungicide and insecticide activity, and different chemical structures. They include triazines, phenylureas, phenoxides, dinitroanilines, triazoles, carbamates, organophosphates and neonicotinoids [72]. The behaviour of these compounds in amended soils can be very variable and has been frequently reported in laboratory experiments, with fewer studies conducted under field conditions [33, 73–75] (Table 2).

Some laboratory studies have been carried out with soils amended in the field to determine the ageing effect of organic amendment on pesticide behaviour. Petter et al. [76] have investigated the long-term effect of biochar (a carbonaceous and porous product generated from incomplete biomass combustion) applied in sandy soils on the kinetics of diuron adsorption and desorption. Biochar's ability to increase the adsorption of diuron and decrease its desorption is due to the increase in total OC and the chemical reactivity of the humic acid and humin fractions. This reduces the potential risk of diuron leaching and the contamination of subsurface water. The addition of biochar to an agricultural soil affects the adsorption, leaching, persistence and enantiomeric composition of the soil residues of two chiral fungicides, tebuconazole and metalaxyl [78]. No significant changes are observed in the scarce mobility and long persistence of tebuconazole when amending the soil with biochar, while this amendment reduces the losses of metalaxyl by leaching and degradation. Furthermore, the final enantiomeric composition of fungicide residues is affected by adsorption to the amendment.

Some studies have addressed the effect of a by-product of olive oil manufacturing usually spread on agricultural lands. Keren et al. [77] have studied the persistence and temporal dynamics of olive mill wastewater (OMW) on the adsorption of diuron by soil sampled from two depths (0–5 and 5–10 cm) in the field, in different time intervals (up to 18 months) following OMW application over various seasons (spring, summer and winter). The bigger effect was on the soil samples from the 5–10 cm layer, which was mitigated with time, although it was season-dependent as the OMW field application in summer led to smaller impacts on diuron adsorption,

Table 2 Effects of organic amendments on the fate of pesticides in soil

Pesticide	Chemical group	Activity	K_{ow}	Water solubility (mg/L)	DT_{50} field (days)	Organic amendment	Process	Reference
Diuron	Phenylamide	Herbicide	2.87	35.6	229	Biochar Olive mill wastes	Adsorption-desorption, Persistence	[76, 77]
Tebuconazole Metalaxyl	Triazole Phenylamide	Fungicide	3.7 1.75	36 8,400	47.1 14.1	Biochar	Adsorption Leaching Persistence Enantiomeric composition	[78]
S-metolachlor	Chloroacetamide	Herbicide	3.4	530	21	Olive mill wastes	Adsorption	[79]
Clomazone	Isoxazolidinone	Herbicide	2.58	1,212	27.3	Olive mill wastes	Adsorption Leaching Persistence	[80]
Metribuzin DCPA (Chlorthal-dimethyl)	Triazinone Benzenedicarboxylic acid		1.75 4.28	10,700 0.21	19 47	Chicken manure and sewage sludge	Dissipation	[81]
Triasulfuron Prosulfocarb	Sulfonylurea Thiocarbamate	Herbicide	−0.59 4.48	815 13.2	38.5 9.8	Green compost	Dissipation Leaching	[74, 75, 82]
Isoproturon Atrazine	Urea Triazine	Herbicide	2.5 2.7	70.2 35	23 29	Manure	Leaching	[83]
Isoproturon	Urea	Herbicide	2.5	70.2	23	Compost of green wastes and sewage sludge	Transport	[84, 85]
Chlorotoluron Flufenacet	Urea Oxyacetamide	Herbicide	2.5 3.5	74 51	59 39	Green compost and spent mushroom substrate	Dissipation Leaching	[35, 86]

as compared to the application in spring and winter. Likewise, Peña et al. [79] have performed laboratory and field experiments to investigate the effects of the OM maturity of two OMWs on the environmental fate of the herbicide S-metolachlor. The soil amendment with fresh and composted wastes under field conditions (over 9 years) has revealed significant increases in the adsorption of S-metolachlor in all the amended soils, with the process being more reversible with the fresh organic amendments than with the composted and field-aged ones. The OMW has also been applied to rice fields under different regimes of irrigation and tillage [80], with the aim being to discover its effect on the environmental fate of clomazone. The evaluation of herbicide adsorption, leaching and persistence has been determined at laboratory scale with soils after different long-term treatments at field scale. The organic amendment is acknowledged as an invaluable strategy for reducing water contamination by clomazone in rice production, especially under traditional tillage and flooding management.

Moreover, pesticide residues in soil and natural resources could also be mitigated in amended soils, although changes in the dissipation of pesticides have to be monitored to characterise pesticide concentration over time. This allows evaluating the persistence of the pesticides applied simultaneously to organic amendments and determining potential residues in runoff and infiltration water or in successive rotational crops. Antonious et al. [81] have reported the effect of chicken manure (CM) and sewage sludge (SS) on the dissipation of metribuzin and DCPA in a native soil. Half-life (DT_{50}) values increase for two herbicides in amended soils, and water infiltration also increases after the addition of the amendments, lowering runoff water volume and herbicide residues following natural rainfall events. The CM and SS amendments reduce pesticide contamination by runoff from agricultural fields, but increase water infiltration towards the vadose zone.

The influence of different factors such as amendment rate, weather, irrigation, pesticide formulation (individual or combined compounds) and application method (single or repeated application) on the dissipation and persistence of the herbicides triasulfuron and prosulfocarb has been evaluated under field conditions by Marín-Benito et al. [74] and García-Delgado et al. [82]. An increase in the persistence of both herbicides has been detected in the soil amended with green compost (GC). However, the individual or combined formulation of pesticides has only affected the dissipation of triasulfuron (decreased when applied as an individual formulation), but not of prosulfocarb due to their competition for adsorption sites. DT_{50} values decrease for triasulfuron but not for prosulfocarb after the repeated application of these herbicides. Furthermore, DT_{50} values decrease with irrigation solely for prosulfocarb but not for triasulfuron, despite its higher water solubility. The results indicate that different conditions could alter herbicide behaviour, making it difficult to forecast their environmental impact.

Marín-Benito et al. [35] have also reported changes in the dissipation of the herbicides chlorotoluron and flufenacet in a sandy-loam soil when amended with GC and spent mushroom substrate (SMS). This is explained by higher herbicide adsorption by the amended soils. The application of SMS and GC to soil slows the dissipation rates of chlorotoluron and flufenacet compared to unamended soils, as previously observed under controlled laboratory conditions [87]. However, the DT_{50} values of chlorotoluron and flufenacet under field conditions are higher than those obtained at laboratory scale by Marín-Benito et al. [87], highlighting the importance of changing environmental conditions in the dissipation process. These changes also affect the formation rates of their metabolites at field scale.

Changes in the leaching of pesticides in soils after applying amendments have also been reported. Tahir et al. [83] have found that a very low risk of isoproturon and atrazine leaching could be achieved by applying a manure amendment when different flood irrigation levels are applied in soil in Pakistan. Their results reveal the effect of pesticide adsorption on soil OM. Filipović et al. [84, 85] have evaluated the heterogeneity due to soil tillage and co-composting of green wastes and sewage sludge, and how it affects transport processes. Amendments modify the soil structure with a major long-term influence on water flow and pesticide dynamics, being specifically influenced by isoproturon distribution and leaching. Both types of compost decreased isoproturon leaching over the six-year experiment.

Changes in leaching have also been recorded for herbicides applied in amended soils. Marín-Benito et al. [75] have evaluated the mobility of triasulfuron and prosulfocarb in an unamended soil and in one amended with GC (two different doses) under non-irrigated and irrigated conditions. The leaching of both herbicides to deeper soil layers is confirmed under all conditions, although larger amounts of residues have been found in the surface layers. The application of GC to the soil increases the persistence of both herbicides and decreases the leaching of triasulfuron. Irrigation affects the leaching of both herbicides in all cases, although other factors such as dissolved organic carbon (DOC) content or soil water storage capacity may be significant in high-dose amended soil.

The results obtained for the mobility of chlortoluron and flufenacet by Carpio et al. [86] in the profile of SMS- and GC-amended soils indicate an increased herbicide retention in the top 10 cm of amended soil by the higher OC content than the unamended soil, and their ability to increase soil water holding capacity and decrease water percolation. The DOC content also facilitates herbicide transport, favoured by the initial soil moisture content and rainfall shortly after the initial application. Nonetheless, higher DOC content in amended soils could play a key role in the dissipation of herbicides in soil profiles by enhancing other processes such as degradation, mineralisation, bound residue formation and/or crop uptake other than leaching below 1 m depth.

These processes affect the behaviour of pesticides, regulating their concentration in the soil solution and determining their bioavailability, conditioning their possible impact on the activity and/or the functioning of soil microbial communities. In fact, the presence of pesticides or their residues in the soil may affect its activity and microbial diversity [88, 89].

5 Fate of Pesticides in Soils Under Conservation Tillage Systems

In addition to crop rotation (see Sect. 6), conservation tillage systems include two other main principles. Firstly, maintaining a permanent plant cover on the soil involving the presence of cover crops and the accumulation of harvested crop residues as mulch during the fallow period in arable crops or between rows of trees in woody crops. At least 30% of the soil needs to be covered to effectively protect it against erosion. However, it is recommendable to leave more than 60% of the soil covered to have almost complete control over the soil degradation process. Secondly, maintaining the soil undisturbed. In practice, this means no-tillage and direct seeding on the mulch [90, 91].

The accumulation of crop residues on the soil surface (mulching) increases the total OM content, reduces surface runoff and soil erosion, captures precipitation, regulates the soil surface temperature, reduces evaporation from the soil surface, increasing soil water content, and controls weeds [90, 92]. Furthermore, the use of cover crops reduces nitrate leaching and increases carbon sequestration [93, 94]. These crops also help to protect water sources and reduce the impact on net global warming, respectively [93–96]. Therefore, their numerous benefits make these cropping systems interesting alternatives to conventional systems [90, 97, 98]. Certain authors have also found changes (both positive and negative from an environmental risk perspective) in the fate of pesticides in soil under conservation tillage systems including intermediate cover crops, no-tillage and the associated presence of crop residues on the soil surface, whereas no effects have been observed by other authors as a result of the influence of other factors such as pesticide and soil properties, weather conditions, their spatial and/or temporal variations or the length of the experiment [36, 99–104].

5.1 Effects of Conservation Tillage Practices on the Fate of Pesticides

Conservation tillage systems may prompt significant changes in physicochemical and hydraulic soil properties, soil temperature and humidity, the abundance of faunal and microbial populations and biological activity, etc., directly or indirectly affecting the behaviour of pesticides in the soil over time [90, 99, 101, 105–107]. It is generally expected that conservation tillage systems such as no-tillage improve macropore connectivity. This increases pesticide leaching and is the main drawback of conservation agriculture practices [99, 107]. In turn, mulch is a lignocellulosic material and could modify pesticide leaching in soils by the adsorption-desorption and degradation of these compounds, with these processes depending on mulch evolution and pesticide properties, as indicated for other materials of a similar nature

[108]. Therefore, a better understanding of the adsorption and degradation processes is called for in conservation agriculture.

Herbicides play a key role in controlling the weeds competing with crops for soil resources because no mechanical destruction of weeds is carried out under conservation tillage systems. Therefore, selective and non-selective herbicides are applied to control the weeds for the corresponding crop and chemically eliminate the cover crops, respectively. Glyphosate is the non-selective herbicide most commonly applied [90], and this compound and its main metabolite, aminomethylphosphonic acid (AMPA), are frequently detected in soil [109] and water sources [110, 111]. Consequently, the behaviour of glyphosate and AMPA has been widely studied within the context of conservation agriculture practices at both laboratory and field scale in recent years [37, 102, 112–115]. This research should be extended to a wider range of compounds to improve our understanding and extrapolate the impact of these conservation agriculture practices on pesticide fate (Table 3).

Pesticide adsorption is considered one of the main processes regulating the fate of these compounds in soils, and it has been widely reported in the literature, with glyphosate as one of the most common target pesticides [16, 112–114], as this process is modified in the presence of cover crop residues. Batch experiments carried out to quantify the influence of the nature of cover crops (oat, turnip rape, red clover and phacelia) and their degree of decomposition on the adsorption of the ^{14}C-herbicides glyphosate and S-metolachlor and the ^{14}C-fungicide epoxiconazole report an increase in the adsorption of pesticides on cover crop residues by increasing their decomposition. Adsorption varies significantly with the type of compound, being additionally influenced by the cover crop's biochemical characteristics [113]. Similar adsorption results have been reported for these three ^{14}C-pesticides in an adsorption-desorption study on maize mulch residues decomposed under laboratory and field conditions [112]. The effect of maize mulch decomposition on pesticide desorption varies. It enhances the desorption of glyphosate in contrast to the decreasing desorption observed for S-metolachlor and epoxiconazole. Mulch characteristics such as aromaticity, hydrophobicity and polarity index are strongly correlated to the soil OC normalised adsorption coefficient (Koc) of the assayed pesticides. An increasing ^{14}C-glyphosate adsorption on four cover crop residues (common vetch, white mustard, hybrid ryegrass and a mixture of common vetch + oat) with increasing decomposition has also been corroborated by Cassigneul et al. [114]. These authors have extended the experiment to a comparative study including ^{14}C-glyphosate degradation on bare soil and soil with a mulch layer of the cited cover crops on the soil surface, observing higher glyphosate adsorption, degradation and mineralisation on/in soil than on/in mulch cover crops. The mineralisation in soil, and/or mineralisation and bound residue formation in decaying cover crops are the herbicide's main dissipation pathways. Differences in composition and availability to microorganisms are used to explain adsorption and degradation levels. Based on a similar combined adsorption-degradation experiment with ^{14}C-S-metolachlor, Cassigneul et al. [16] have concluded that this herbicide's behaviour in conservation agriculture is determined by the percentage of herbicide intercepted by cover crop residues and their state of decomposition. The adsorption process has the same

Table 3 Effects of conventional and conservation tillage practices on the fate of pesticides

Pesticide	Chemical name	Activity	K_{ow}	Water solubility (mg/L)	DT_{50} field (days)	Factor	Process	Reference
Glyphosate	Phosphonoglycine	Herbicide	−3.2	10,500	23.79	No-tillage and conventional tillage	Leaching	[36, 37]
S-metolachlor Glyphosate	Chloroacetamide Phosphonoglycine	Herbicide	3.4 −3.2	530 10,500	21 23.79	Rainfall regimes and mulch decomposition	Dissipation leaching	[102]
^{14}C-nicosulfuron	Sulfonylurea	Herbicide	0.61	7,500	19.3	Conventional agriculture (tillage, bare soil and monoculture) and conservation agriculture (no-tillage, cover crops and crop rotations)	Adsorption Degradation	[103]
Glyphosate	Phosphonoglycine	Herbicide	−3.2	10,500	23.79	No-tillage and conventional tillage	Leaching	[104]
^{14}C-Glyphosate ^{14}C-S-metolachlor ^{14}C-Epoxiconazole	Phosphonoglycine Chloroacetamide Triazole	Herbicide Herbicide Fungicide	−3.2 3.4 3.3	10,500 530 7.1	23.79 21 97.7	Decomposition degree of maize mulch residues	Adsorption-desorption	[112]
^{14}C-Glyphosate ^{14}C-S-metolachlor ^{14}C-Epoxiconazole	Phosphonoglycine Chloroacetamide Triazole	Herbicide Herbicide Fungicide	−3.2 3.4 3.3	10,500 530 7.1	23.79 21 97.7	Nature and decomposition degree of cover crops (oat, turnip rape, red clover and phacelia)	Adsorption	[113]
^{14}C-glyphosate AMPA	Phosphonoglycine Metabolite	Herbicide	−3.2	10,500	23.79	Nature and decomposition degree of cover crops (vetch, white mustard, hybrid ryegrass and vetch + oat)	Adsorption Degradation mineralisation	[114]
^{14}C-S-metolachlor S-metolachlor-ESA S-metolachlor-OA	Chloroacetamide Metabolite Metabolite	Herbicide	3.4	530	21	Nature and decomposition degree of cover crops (vetch, white mustard, hybrid ryegrass and vetch + oat)	Adsorption Degradation Mineralisation	[16]
^{14}C-glyphosate AMPA	Phosphonoglycine Metabolite	Herbicide	−3.2 −1.63	10,500 1,466,561	23.79 419	Trapped herbicide in oilseed rape residues	Persistence Mineralisation	[115]
Nicosulfuron Mesotrione Metaldehyde	Sulfonylurea Triketone Cyclo-octane	Herbicide herbicide Molluscicide	0.61 0.11 0.12	7,500 1,500 188	19.3 5 5.1	No-tillage and conventional tillage	Leaching	[116]
Imazapyr	Imidazolinone	Herbicide	0.11	9,740	11	No-tillage and conventional tillage	Adsorption	[117]

affect, and the degradation of S-metolachlor indicates that DT_{50} lasts 23 days in bare soil, and 9, 15, 39 and 25 days in cover crops (ryegrass and vetch + oat mixture), ordered by increased decomposition state (0, 6, 28 or 56 incubation days) at the time of application. Cassigneul et al. [16] have again attributed these results to the proportion of herbicide intercepted by the cover crop residues, and to higher levels of OM and microbial activity in less decomposed cover crop residues, as compared to more decomposed ones.

A potential source of soil and water contamination by pesticides that should not be obviated within conservation agriculture including cover crops and the continuous coverage of the soil surface by plant residues is the fraction of pesticides intercepted and absorbed by the leaves of weeds and/or crops that are then returned to the soil during the plant cycle (via leaf senescence) or after harvest (as crop residues). The fate of glyphosate associated to its interception and absorption by plant residues has been assessed by Mamy et al. [115] through a laboratory study with ^{14}C-glyphosate applied on oilseed rape and on soil. The evaluation of the mineralised, extractable and non-extractable fractions of the herbicide and its metabolite AMPA show that the incorporation of glyphosate into oilseed rape residues hinders its mineralisation in soils and increases its persistence and that of AMPA in soils.

Additional studies involving hand-packed soil columns covered with a mulch of maize and lablab residues have helped to improve our knowledge on the effect that pesticide properties, precipitation regimes and mulch decomposition have on the dissipation and leaching of S-metolachlor and glyphosate [102]. The authors have simulated a light but frequent rainfall (LF) and a less frequent but more intense rainfall (HI) in the columns. Under these conditions, more than 50% of the pesticide applied is retained by the decomposing mulch on the soil surface. More humid surface conditions, under which mulch decomposition is faster, explain quicker S-metolachlor dissipation in mulch residues under LF, which also enhances the formation of metabolites (S-metolachlor-ESA, S-metolachlor-OA and AMPA) of both herbicides. The leaching behaviour of S-metolachlor and its metabolites is controlled by the precipitation regime, whereas glyphosate remains in the surface soil layer because of its strong adsorption capacity, and small amounts of AMPA leach down independently of the precipitation regime.

The aforementioned studies focus on how the interception of pesticides by cover crops impacts on the fate of these compounds in conservation agriculture. Another important aspect within the comparison of conventional and conservation agriculture is the effect on pesticide behaviour of the corresponding tillage or no-tillage of soil. Cueff et al. [103] have recently used controlled laboratory conditions to study the adsorption and degradation of the herbicide ^{14}C-nicosulfuron in 90-cm soil profiles of Stagnic Luvisol and Vermic Umbrisol managed for more than 10 years under either conventional agriculture (CT) (tillage, bare soil and monoculture) or conservation (NT) (no-tillage, cover crops and crop rotation). The authors have not found significant differences in the behaviour of nicosulfuron, especially under contrasting types of agricultural management. No significant difference in herbicide adsorption behaviour has been observed either between the two types of agricultural management studied, probably due to the low adsorption affinity of nicosulfuron for soil components, including OC. The degradation results show that nicosulfuron mineralisation is influenced more by soil depth than by the type of agricultural management. The formation of non-extractable residues is one of the main nicosulfuron dissipation pathways, especially for NT systems. In the undisturbed columns sampled in these same soils, Cueff et al. [116] have reported that NT improves pore network connectivity, and the water and pesticide (nicosulfuron, mesotrione and metaldehyde) flow becomes predominantly vertical. However, transfer by drainage is strongly limited in ploughed Stagnic Luvisol by hydraulic discontinuity due to tillage operations. In contrast, Okada et al. [104] have not observed any significant effect of the tillage system in the losses of glyphosate by leaching through a laboratory study also involving undisturbed soil columns (15-cm long) from three different long-term field trials (more than 16 years) under NT and CT practices. It should be noted that this lack of significance could be due to the low mobility observed for the herbicide (retained mainly in the top 5 cm of the soil columns), which is influenced mainly by the compound's strong adsorption in all soils. The authors have observed a positive influence of soil clay content and cation exchange capacity in herbicide adsorption, with soil pH and phosphorous content having a negative influence. A similar effect (equivalent leaching) has been found for the herbicide imazapyr in undisturbed columns of two soils with different physical–chemical properties, both subject to long-term (7 or 15 years) CT and NT systems [117]. In this case, the no-adsorption and weak adsorption of imazapyr determined, respectively, in CT and NT soils by batch studies explain the equivalent herbicide leaching observed under both tillage systems.

The influence of CT and NT soil management on pesticide leaching has also been compared at field scale. Soracco et al. [36] have compared the temporal evolution of physical and hydraulic soil properties under CT and NT practices, and their relationship with the vertical mobility (0–40 cm) of glyphosate applied three times during a soybean cycle. The authors have reported strong herbicide retention in the top 20 cm of both soil managements. However, the higher saturated hydraulic conductivity, total macroporosity and effective macroporosity values determined in the CT system prompt higher temporal variation in herbicide leaching under this tillage practice. The vertical mobility of glyphosate under NT seems to be limited by low values of saturated hydraulic conductivity, total macroporosity and effective macroporosity. Therefore, the temporal variation in glyphosate vertical transport is explained by the temporal variation in the physical and hydraulic soil properties studied. Villarreal et al. [37] have recently focused on glyphosate accumulation and mobility throughout the soil profile (0–30 cm) during a crop cycle in two different textured soils (silty loam and sandy loam) under NT and CT systems. They have reported higher values of available water content and lower values of saturated hydraulic conductivity in soils under NT compared to CT. This influences glyphosate behaviour, whose persistence and leaching are related to soil water retention and hydraulic conductivity, respectively. The authors conclude that fine textured soils, especially under NT, with high water retention and low hydraulic conductivity and low pore connectivity, are more susceptible to glyphosate accumulation. However, high hydraulic conductivity may enhance glyphosate leaching, as observed under CT for the silty loam soil.

6 Effects of the Fate of Pesticides in Soils in Rotational Crops

Crop rotation is a management practice that seeks to maximise productivity per unit area, optimising the use of resources. It consists of a succession of different crops in the same soil over time that allows increasing the residual nutrients in the soil, which remain available for the next rotational crop. This allows improving the soil's natural fertility and its biodiversity, as well as reducing both the incidence of pests and diseases by breaking cycles that are maintained in monoculture systems and the need for pesticide application and herbicides for weed control [90]. Weed competition with crops can be restricted by maintaining a live soil cover through crop rotations, thereby limiting weed growth. Cover crop rotations with leguminous and oilseed species, for example, provide additional benefit of dietary diversity (for both animals and humans), as well as improve biological nitrogen fixation to the soil in semi-arid regions [118]. However, the presence of herbicide residues in the soil from a previous crop could affect rotational crop yields. Herbicides with a different chemical structure, mainly involving triazine, phenylurea, sulphonylurea, imidazolidinone and dinitroaniline families, are applied to cereals, cotton, rice, etc. under rotational crops. These compounds' characteristics, such as water solubility, pKa, K_{ow} or DT_{50} vary in a wide range [72]. Some studies have indicated that the presence of herbicide residues (some from these different families) in the soil, due to their long persistence under certain conditions, could cause negative effects on subsequent crops [119, 120]. The persistence of the compounds used as herbicides has been well established when the product is commercialised, but it could be modified by environmental factors, causing the product to continue in the soil for longer than the marked safety period. This period is determined in specific scenarios for registered pesticides, but they could change for soils with different properties and weather conditions than those assayed.

An evaluation of the fate of herbicides in the soil in crop rotation systems is absolutely necessary to optimise their efficiency and minimise their damage on subsequent crops. Herbicides have to be sufficiently persistent to control weeds, but then they should degrade rapidly to avoid harming any subsequent non-tolerant crops [121, 122]. Therefore, in contrast to Sects. 4 and 5 designed to assess how different agricultural practices modify the fate of pesticides, including their persistence in soils, this section focuses on the consequent impact of pesticide residues on subsequent crops and the factors influencing their persistence under the crop rotation arrangement frequently implemented in conservation tillage systems [90], and which may also be practiced in combination with the application of organic amendments [58].

The chemical herbicide's characteristics and its rate of application are among the factors influencing its persistence in the soil after its application and its residues' potential for carryover injury to rotational crops. These are compounded by physicochemical and biological soil characteristics, environmental conditions or the management practices affecting the dynamic of herbicides in soils [123–126].

Rotations of wheat or barley/rapeseed, sunflower or leguminous species are frequent under rainfed conditions due to the eco-benefits of increased nutrient management and the reduced need for nitrogen fertilisers [127]. The herbicides used on cereal crops belong to different chemical groups, and the selection of these compounds is essential for their future persistence or carryover effect (Table 4). However, some phytotoxic effects have been reported in sunflower crops caused by residues of herbicides such as metsulfuron-methyl belonging to the sulfonylurea group applied to cereals in different regions of Spain [128, 129]. The effect of soil pH on herbicide persistence is known to play an important role for sulphonylureas and imidazolinones. The soil persistence of imazaquin and imazethapyr is greater in low pH soils as a result of the higher adsorption to soil colloids, which means lower availability for microbial degradation. In Argentina, the introduction of imidazolinone-resistant sunflowers constitutes a major technological advance for weed control, although it is a concern for farmers that herbicide carryover may affect the growth of cereals sown during the autumn and winter. Scursoni et al. [130] have found that the mixture of imazamox plus imazapyr is safer for rotational crops than imazapyr applied alone because of the reduced rate of imazapyr in the mixture. In addition, barley is more sensitive to imidazolinones, particularly imazapyr, than the other winter cereals (oat and wheat).

The effect of environmental conditions, such as rainfall after the application of herbicide, affects the behaviour of these compounds in soils and then their persistence and carryover. Cornelius and Bradley [131] have reported variable effects on subsequent autumn-seeded cover crop species when several commonly used herbicides such as pyroxasulfone, imazethapyr, fomesafen and flumetsulam are applied to corn and soybean. Their results indicate that the severity of the damage to cover crops depends on the weather, the species and the specific herbicide combination. The risk of the soil-residual herbicide fluridone applied to other crops such as cotton injuring the subsequent growth of wheat, corn, soybean, rice, grain sorghum and sunflower has been evaluated by Hill et al. [132]. Multiple rates of fluridone have been assayed at four irrigated locations across Arkansas, and injury to a rotational wheat crop was more likely than to other rotational crops following its application. For other rotational crops in Mississippi, Lawrence et al. [124] have indicated that only clomazone should be used as an autumn-applied residual herbicide treatment for targeting glyphosate-resistant Italian ryegrass before seeding rice, while applications of pyroxasulfone, S-metolachlor and trifluralin should be avoided.

Other studies on the efficacy on soybean of pre- and post-emergence herbicides with residual activity (trifluralin, diclosulam, imazaquin, imazethapyr and cloransulam) have not found any effect on the yield of the corn subsequently cultivated [122]. Research conducted by Grey et al. [133] on pyrasulfotole applied to wheat in Georgia has not found any adverse effect on peanut and tobacco grown in

Table 4 Characteristics of herbicides used in crop rotation

Pesticide	Chemical name	Activity	K_{ow}	Water solubility (mg/L)	DT_{50} field (days)	Crop rotation	Reference
Trifluralin	Dinitroaniline	Herbicide	5.27	0.221	170	Soybean/corn	[122]
Diclosulam	Sulfonanilide		0.85	6.32	20		
Imazaquin	Imidazolinone		−1.09	102,000	4.3		
Imazethapyr	Imidazolinone		1.49	1,400	51		
Cloransulam	Sulfonanilide		−0.36	184	10		
Clomazone	Isoxazolidinone	Herbicide	2.58	1,212	27.3	Glyphosate-resistant Italian ryegrass/rice	[124]
Pyroxasulfone	Pyrazolium		2.39	3.49	22		
S-metolachlor	Chloroacetamide		3.4	530	21		
Trifluralin	Dinitroaniline		5.27	0.221	170		
Metsulfuron methyl	Sulfonylurea	Herbicide	−1.87	2,790	13.3	Cereals/sunflower	[128, 129]
Imazethapyr	Imidazolinone	Herbicide	1.49	1,400	51	Sunflower/wheat, barley and oat	[130]
Imazaquin	Imidazolinone		−1.09	102,000	4.3		
Pyroxasulfone	Pyrazolium	Herbicide	2.39	3.49	22	Corn/soybean	[131]
Imazethapyr	Imidazolinone		1.49	1,400	51		
Fomesafen	Organochlorine		−1.2	50	86		
Flumetsula	Cyclodiene		0.21	5,650	45		
Fluridone	Unclassified	Herbicide	1.87	12.3	21	Cotton/winter wheat, corn, soybean, rice, grain sorghum and sunflower	[132]
Pyrasulfotole	Pyrazolone	Herbicide	−1.362	69,100	55.5	Winter wheat/peanut and tobacco	[133]
Florpyrauxifen-benzyl	Pyridine	Herbicide	5.46	0.011	150	Rice/soybean	[134]
Fenpyrazone	Benzoylpyrazole	Herbicide	–	–	–	Maize/winter wheat, garlic and spinach	[135]

rotation because pyrasulfotole is adsorbed by the soil and does not readily desorb back into the aqueous phase.

New compounds with herbicide activity have now been developed to avoid carryover effects on rotational crops under different conditions. Miller and Norsworthy [134] have investigated the potential carryover effect on soybeans of a new active ingredient, florpyrauxifen-benzyl, developed for use as an herbicide for rice crops. Based on the rates evaluated and the environmental conditions during the experiments, these authors indicate that a relatively short replant interval for soybean after application is supported compared to other herbicides commonly used on rice, such as triclopyr and quinclorac. Wang et al. [135] have conducted an experiment on the North China Plain to evaluate the response of successive rotational crops to the new herbicide fenpyrazone, applied to preceding summer maize fields relative to other herbicides such as mesotrione or imidazolinone compounds with known carryover. The authors report that winter wheat, garlic and spinach grow safely following fenpyrazone post-emergence application at the recommended rate to preceding summer maize, although further research is necessary on its effects on successive rotational crops over a wider range of soil types and under different climate and cultivation systems.

A study carried out by Rector et al. [126] has determined the potential of 30 different residual herbicides commonly used in summer cash crops in Virginia to persist in the soil and injure subsequent cover crops. The results obtained indicate that herbicide persistence varies with location (soil type) and year (weather). The impact of soil texture on herbicide carryover potential has also been reported, although it is suggested that the interaction between the herbicide, climate and all the factors associated with the herbicide's ability to persist in the soil is complex, and localised research is needed. Similarly, Palhano et al. [125] have conducted a study on the sensitivity of cover crops to a low rate of soil-applied herbicides on a silt loam soil following the corn harvest, reporting that the results cannot be generalised over broad production practices, environments and soils, because all these factors are probably linked to geographical regions. These authors indicate that the "sensitivity trial" does not adequately assess the risk of carryover, but does help to refine the list of herbicides that should be evaluated for carryover to cover crops. Wallace et al. [136] have also reported the increasing interest in the use of intercropping strategies to establish cover crops in corn cropping systems, although cover crop growth and its response to herbicide treatments vary across sites and years.

Further research is called for by different authors to identify broad-spectrum weed control programmes that are compatible with inter-seeding cover crop mixtures. It is therefore important to identify herbicide options that overcome the trade-off between weed suppression and cover crop performance. In some cases, growers may be willing to accept moderate levels of cover crop damage in order to balance weed management and conservation goals.

7 Modelling of Pesticide Fate Under Different Soil Management Practices

In line with previous sections, there are numerous single and potential combinations of agricultural practices for more sustainable global agriculture. There is a wide variety of agricultural-pedoclimatic scenarios where pesticide application demands an ideal assessment of their known environmental fate and risks through previous in situ experiments to safely extend and normalise these practices. However, this option is prohibitive in costs and time, which is not in keeping with current and future agricultural, social and environmental demands. In this context, pesticide fate models have become useful tools for assessing and predicting pesticide concentrations in air, soil, water and plants [137].

A large number of models have therefore been developed since the 1980s to evaluate the fate of pesticides in the environment for both research and registration purposes [12, 138]. These models consider most of the processes involved in the fate of pesticides in the environment (adsorption, degradation, leaching, volatilisation, absorption by plants, erosion and/or runoff) and allow integrating climate, pesticide and soil characteristics, as well as agricultural practices (Fig. 3). It should be noted that the application and development of these pesticide fate models have generally evolved in step with agricultural practices. Since their first versions at the end of last century and for a long time, process-based numerical models have been mainly used to successfully evaluate the behaviour of pesticides influenced by different factors, including pedoclimatic conditions, under conventional agricultural practices. The initial modelling exercises at field scale have focused largely on the ability of pesticide fate models to individually reproduce the experimental leaching and persistence behaviour of pesticides in the corresponding scenarios [139–141]. The development and availability of multiple models has later led to a comparison of the performance of different models to assess the fate of pesticides in the same scenario [142–144], even describing the application of the principles of good modelling practice [137].

The next objectives of modelling studies have involved testing sensitivity and uncertainty analyses, as well as detecting sources of error in model predictions of pesticide fate [145–147]. Once the advantages and limitations of each pesticide fate model have been identified, modelling exercises have been used to simulate the impact of more specific factors on pesticide behaviour, such as irrigation practices [148, 149], precipitation patterns [150], greenhouse conditions [151], etc. In recent years, pesticide fate modelling under conventional agricultural practices has considered factors such as the aged adsorption of pesticides [152], tropical weather conditions [153], climate change [154], scenarios' scale [155–157], the optimisation of irrigation and pesticide application patterns [158–160], among others.

Accordingly, pesticide fate under conventional agricultural practices has therefore been largely simulated. However, the representation of conservation agricultural practices, such as organic amendment, tillage/no-tillage, crop rotation, cover crops, mulching, etc., remains incomplete in pesticide fate models [161]. As a result, very few modelling studies have been carried out under these types of scenarios. In recent years, different options have been explored to adapt pesticide fate models to conservation agricultural practices or to take into account their effects on pesticide dynamics, as in general their codes have not initially been designed to do so. In this respect, Marín-Benito et al. [34] have assessed the ability of PRZM [162] and MACRO [163] models to simulate chlorotoluron and flufenacet concentrations in the soil profiles (0–100 cm) of an unamended agricultural soil (S), and one amended with spent mushroom substrate (S + SMS) or (S + GC) determined in a two-year field experiment. While no calibration is needed to suitably reproduce the vertical distribution of the herbicides in the unamended soil profile, a calibration step (different for each herbicide and model) has been implemented to obtain an adequate simulation of herbicide mobility in amended soils. The calibration affects DT_{50} degradation coefficients and/or K_d adsorption of herbicides, being based on the initial DOC content of amended soils, assuming that the DOC of the SMS and GC amendments enhances their bioavailability for degradation and their mobility through the amended soil profiles via the formation of herbicide-DOC mobile complexes by decreasing the effective adsorption of herbicides. The authors conclude that both models could be successfully used as predictive tools to avoid groundwater pollution by herbicides in amended soils, although further modelling studies should be carried out on other pedoclimatic and pesticide-organic residue combinations and for longer periods in order to optimise the application rates of organic residues and prevent water pollution.

Marín-Benito et al. [35] have used the MACRO model to perform a complementary modelling of the persistence of chlorotoluron and flufenacet in the same unamended and amended soil scenarios. The reasonable agreement between the herbicides' experimental and simulated dissipation data highlights MACRO's ability to predict the remaining herbicide amounts in the root zone of amended soils and its potential use for assessing whether the application of herbicides in amended soils may damage subsequent crops, as well as optimise herbicide doses, which could be of great interest in crop rotation (see Sect. 6).

In the context of water quality conservation, the MACRO model has also been used to simulate a hypothetical attenuation (without comparing with experimental data) of chlorpyrifos leaching in two productive arid soils under flood irrigation after the incorporation of OM into the soil [158]. The promising simulation results point to one of the future applications of pesticide fate models in amended soil scenarios.

The performance of the pesticide fate model HYDRUS [164] for predicting pesticide behaviour in an amended soil has been also tested. Filipović et al. [84] have modelled the impact of soil heterogeneity on the water flow and isoproturon dynamics resulting from mouldboard ploughing and the application of compost amendments (co-compost of green wastes and sewage sludge applied once every 2 years) in a long-term field experiment (15 years) based on a plot cultivated with a biannual rotation of winter wheat–maize. Neither the laboratory-measured isoproturon fate parameters nor the independently-derived soil hydraulic parameters determined in the four zones identified in the ploughed layer (compacted clods, non-compacted soil, inter furrows and the plough pan) allowed reproducing the six-year field dynamics of water and isoproturon with the HYDRUS-2D model [164] without calibration. The authors have only managed to satisfactorily reproduce the water and isoproturon dynamics (except when preferential flow events are observed) after the optimisation of soil hydraulic properties and the herbicide degradation rate. The calibration of the isoproturon degradation rate assumes the additional degradation of the herbicide in solid (adsorbed) phase to that considered in liquid phase. In a similar study extended to plots amended with the previous co-compost of sewage sludge and green wastes, with a municipal solid waste compost and without amendments (control plot), Filipović et al. [85] have again had to calibrate soil hydraulic properties to satisfactorily simulate the registered water dynamics, and the water and isoproturon flows collected in passive capillary-wick lysimeters installed at the 45-cm depth. In this case, a temporal variation in the herbicide degradation rate is assumed to reproduce its experimental leaching behaviour with the HYDRUS-2D model.

Other authors have also compared the ability of the HYDRUS code to reproduce water and pesticide dynamics in soil under no-tillage and/or conventional tillage considering constant or time-variable hydraulic properties [165, 166]. Alletto et al. [165] have improved water dynamics modelling in a conventionally tilled soil when a temporal variation in physical properties (saturated hydraulic conductivity, bulk density and soil water retention) during a maize-growing season has been optimised and considered in the HYDRUS 2-D model. Although no pesticide dynamics are simulated, the authors stress that time-variable physical soil properties should be taken into account in modelling to correctly assess both water and pesticide dynamics in soils. In addition, Alletto et al. [165] have reported modelling results under a conventional tillage system, arguing for the need to extend this type of studies to other kinds of agricultural management because the temporal variation in physical soil properties is heavily influenced by it, especially by the tillage system, which remains poorly characterised. Villarreal et al. [166] have fairly accurately predicted experimental glyphosate and AMPA distribution throughout the soil profile with the HYDRUS 1-D model [164] under both no-tillage and conventional tillage systems. However, they have not observed any improvement in the simulation performance after considering constant or time-variable hydraulic properties.

Very few models have been designed and/or adapted to consider the effects of cover crops, mulching and/or other agricultural conservation practices on pesticide environmental fate [167–170]. In fact, the coupling of existing models or implementing new modules on them has been the way to represent these complex scenarios in most cases. Queyrel et al. [169] have developed the STICS-Pest model after adding a pesticide-module to STICS, a crop model for simulating various agricultural practices including rotation, tillage, mixed crops, management residues, etc. [171]. They have obtained promising results in the initial simulations of bentazone, isoproturon and atrazine leaching in different scenarios. Other authors have assessed the performance of the sequential use of the STICS crop model and of the MACRO pesticide fate model to simulate water percolation and imazamox and S-metolachlor leaching in two six-year field trials under monoculture or crop rotation systems in contrasting pedoclimatic conditions [167], and the simulation results have also been compared to those simulated by the single MACRO model. The authors have found a satisfactory correlation between predicted and measured data with STICS-MACRO, which is similar to or better than that of MACRO as a result of a more accurate estimation of crop transpiration, water balance and herbicide interception induced by improved crop growth simulation. The study's results show that STICS-MACRO is a new and promising tool for improving the assessment of the environmental risks of pesticides used in complex cropping systems. A subsequent sensitivity analysis of this STICS-MACRO model has identified cropping practices that reduce pesticide losses [172]. The modelling study shows that the effects of cropping practices on pesticide losses could be more relevant than those of soil, crop or climate in some contexts. In this sense, mulch could increase pesticide leaching in relation to its effect on soil moisture, whereas a decrease in pesticide concentrations in water has been simulated under soil tillage.

Marín-Benito et al. [168] have developed an approach to model the effects of mulch and intermediate cover crops (a mixture of oat, phacelia and vetch) on the water dynamics and S-metolachlor leaching with the MACRO model. Their strategy consists of the following: (1) considering the mulch as a high organic soil layer with its own physical, hydrodynamic and pesticide-reactivity and (2) introducing a correction factor of the potential evapotranspiration to take into account the lower soil evaporation due to the presence of the mulch. This strategy enables MACRO to fairly accurately simulate water percolation and herbicide leaching, although its performance when reproducing the soil water content is poor. The study's most important conclusion is that the model's parameterisation remains limited to the scenario assayed and cannot be proposed for a predictive use of the model. This approach therefore needs to be tested against other pedoclimatic-pesticide-crop mulch combinations in order to use the model as a predictive tool.

8 Research Gaps and Future Improvements

All the studies cited above refer to modelling within a research context. However, these pesticide fate models are also used for registration purposes. Simulation models are therefore a useful tool for supporting authorities in their decisions concerning the approval of pesticide registration. In this regulatory context, four models are recommended by FOCUS (FOrum for the Co-ordination of pesticide fate models and their USe) for risk assessment during pesticide registration at European level [12]: MACRO [163], PEARL [173], PELMO [174] and PRZM [162]. However, conservation agricultural practices such as the addition of organic amendments, mulching, cover crops, etc. are not considered within the 125 groundwater scenarios considered as representative of European agricultural practices, and therefore their impact on the leaching of active substances is obviated in the simulations conducted for registration purposes [12, 13]. According to the potential modification of the fate of pesticides under the different soil management practices explained in Sects. 4–6, they should be taken into consideration in risk assessment and registration procedures. Some of the modelling studies previously cited indicate the need for a calibration step to suitably describe the pesticide leaching behaviour observed in the field. However, as the calibration of pesticide parameters is not possible when these models are used for risk assessment in pesticide registration procedures, some authors have suggested the possible solution of implementing new modules in these pesticide fate models to control, for instance, the effect of DOC from organic amendments on pesticide adsorption and degradation, or the effect of mulch on soil evapotranspiration [34, 168]. This model code optimisation, together with other model applications described in Sect. 7, should be considered as a potential pathway towards which future modelling efforts might most profitably be directed.

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Biopurification Systems: Current Advances and Future Prospects of On-Farm Biodegradation of Pesticides

Carlos E. Rodríguez-Rodríguez, Juan Carlos Cambronero-Heinrichs, Víctor Castro-Gutiérrez, and Gonzalo R. Tortella

Contents

Abstract The mishandling of agrochemical residues in agriculture exerts an important risk for the environment due to point source contamination. To minimize environmental exposure to pesticides, biopurification systems (BPS) have been developed as a biotechnological tool for the on-farm treatment of pesticide-containing wastewater of agricultural origin. Although efficient in the removal of diverse pesticides, highly recalcitrant compounds have shown poor elimination in

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BPS; moreover, the performance of BPS still needs to be evaluated for many agrochemicals and their sustainability should be assessed in real pesticide application cycles for specific crops. Recent studies describe the use of BPS for the removal of antibiotics of agricultural use; this approach required a previous assessment on the impact of antibiotics on BPS performance, which in most cases has revealed the absence of significant adverse effects on pesticide removal. Similarly, novel applications propose the potential use of BPS for the removal of pharmaceuticals from polluted matrices such as water or sludge. The degradation processes taking place within BPS and their link with the resident microbial communities have been scarcely studied to date; they are critical to achieve proper design and optimization of these systems. This chapter covers general aspects of BPS and their application scope to pesticides; special attention is given to novel topics such as the treatment and effect of antibiotics from agricultural wastewater and pharmaceutical-containing matrices, as well as the description of microbial communities within BPS.

Graphical Abstract

Keywords Antibiotics, Biobeds, Biopurification systems, Pesticides, Wastewater

1 Biopurification Systems: Tools for the Treatment of Pesticide Containing Wastewater of Agricultural Origin

Biopurification systems (BPS) are low-cost, simple, and effective tools that play an important role in the removal of pesticide-contaminated wastewater and the detoxification of point sources of pesticide residues, which represent potential risks as agents of water pollution [1, 2]. In general, a BPS is an ex situ bioremediation treatment technology, consisting of a solid-phase bioreactor or a composting facility, whose prophylactic purpose is to treat water contaminated with agrochemicals used in farming, aiming at their accelerated removal [3–6].

The inadequate management of pesticides and other farming chemicals may result in the exposure of soil, surface water, and groundwater to these residues [3, 7]. Hence, the main objective of a BPS is to minimize the contamination risk produced by point sources of pesticide pollution. These tools are devices intended to retain and degrade pesticide spills occurring during the filling of spraying equipment or tanks, resulting from leakages, caused by incorrect disposal of machinery-washing residues during and after the application process, and those comprised of wastewater from the rinsing of pesticide containers [1, 8–11].

BPS originated during the 90s in Sweden under the name of "biobeds" and in subsequent decades, this simple and effective strategy attracted the attention of many countries, mainly located in Europe [12, 13]. The biobed system has been adapted multiple times and even renamed as biomassbed in Italy, biofilter in Belgium, and Phytobac and biobac in France, for instance [1, 9]. The simplicity of BPS configurations has made them suitable for emulation in developing countries in Latin America, for example, Guatemala, Costa Rica, Chile, Peru, Ecuador, Brazil, and Argentina [1, 5, 10, 11].

These BPS or "biobeds" consist of a highly active biological biomixture confined in a container or excavation. The original European "biobed" consisted of three components: a clay layer at the bottom (to avoid contaminant breakthrough); topped by a mixture of peat, straw, and soil (1:2:1), known as biomixture; and a grass layer covering the surface, which helps to maintain the correct humidity, while also working as a useful indicator of pesticide spills [1, 12, 13]. Costa Rican adaptations of BPS, for example, are limited to a plastic container (without the clay layer) that functions as an impermeable material, and usually do not include the grass surface layer (Fig. 1a) [5, 14], while on the contrary, other container-scale biobeds in Brazil employ the grass cover (Fig. 1b); an excavated biobed is also shown in Fig. 1c. The biomixture represents the biologically active core of the BPS; this matrix can be prepared employing locally available materials, and adjustments to the original composition respond to material availability. For instance, alternative lignocellulosic substrates, other than straw, such as coconut fiber, barley husk, rice husk, oak husk, vine-branches, pine sawdust, and even newspaper, have been used; similarly, the substitution of peat by compost has resulted in the production of efficient biomixtures [5, 15–20]. Once spilled in the BPS, the vast majority of pesticides are retained in the upper parts of the biomixture and removed within 1 year [1, 9]. However, many pollutants have demonstrated to be highly recalcitrant (see Sect. 2).

The biomixture promotes the adsorption of organic compounds and their further removal by degrading microbial communities [1, 4]. The three main elements that compose the biomixture are: (1) a lignocellulosic substrate that promotes the growth of microbes, especially white-rot fungi; during the transformation of lignin-rich substrates, these organisms produce promiscuous enzymes (such as laccases and lignin peroxidases) characterized by their high and broad oxidative capacity that may enhance the removal of pesticides and many other organic pollutants [4, 21]; (2) a humic component such as peat or compost that regulates pollutant retention and maintains the BPS moisture, while simultaneously potentially providing degrading

Fig. 1 Different configurations of biopurification systems: container-scale biobed in Costa Rica (without grass cover; **a**) and Brazil (with grass cover; **b**); excavated biobed in Brazil (**c**)

microbial communities; and (3) soil, preferably pre-exposed to pesticides, from a farming site. Soil is the main source of the active degrading microbial populations which contain a plethora of gene products for the removal of organic contaminants. As these communities have been previously exposed to the pollutants, the use of primed soil usually results in an accelerated pesticide removal within the BPS, analogous to environments exposed to antibiotics, where higher frequencies of antibiotic resistant genes are developed [1, 2, 4, 9, 11].

Some abiotic factors have to be taken into account to maintain the proper functioning of the biobeds. First of all, due to degradation of the lignocellulosic material, the carbon content in the biomixture decreases with time; consequently, the biomixture in the BPS should be regularly replaced. Even so, in the case of European biobeds, it is estimated they can last for up to 8 years under functional conditions [1]. Furthermore, the material removed from the biobed may contain residues of pesticides, and a subsequent composting process of 1 year is recommended to reduce the levels of pollutants under detectable limits in this waste [9]. Temperature is also a very important parameter, quicker pesticide removal can be recorded in warmer environments, while removal might substantially decrease in temperate regions during winter [1, 18]. Finally, water balance is a very delicate variable in BPS, as biobeds saturated with water will maintain primarily anaerobic conditions that are not suitable for the removal of pesticides; in this respect, some authors recommend using caps or roofing on biobeds to avoid rainfall saturation, which may also result in high risk of spilling pesticides [1, 9, 11, 18].

2 Application Scope: Removal of Pesticides from Diverse Chemical Families

A plethora of active ingredients are currently used in agriculture for the control of several plant pests such as insects, bacteria and fungi, nematodes or viruses. These compounds are grouped according to their mode of action, target pest, or by chemical group. Compounds grouped in the same family usually have a similar chemical core structure, and therefore similar chemical properties, including toxicological features, and their level of resistance to biodegradation.

As previously mentioned, BPS were designed to treat pesticide residues to avoid point source contamination. Therefore, given that under field conditions diverse pesticides from different chemical families are applied, the degradation capacity of BPS must be wide enough to be able to degrade different active ingredients (herbicides, insecticides, fungicides), sequentially applied alone or in mixture. Since BPS were first developed, degradation studies in these systems have included individual pesticides at different concentrations [22–24], but also mixtures of pesticides from the same chemical family [25] or from different chemical classes [26–28], including studies with real wastewater containing more than 50 active ingredients belonging to many chemical families [28].

Early studies report that soil degradation of pesticides such as atrazine [29] is fast, and the removal rate can increase rapidly when applied repeatedly due to adaptation of the microbiota [30] in a process known as accelerated pesticide degradation [31]. Similar results have been reported for chlorpyrifos, metolachlor, and terbuthylazine in soil, among many others [32, 33]. In contrast, other pesticides such as glyphosate show fast initial degradation, which decreases over time due to strong adsorption to the soil matrix [34]. Additionally, it has been reported that the presence of pesticide mixtures in soil can affect their degradation rate [35], either favoring or decreasing the removal. Moreover, it is well known that degradation rate, movement, distribution, and adsorption/desorption processes of pesticides in soil are governed by physicochemical properties of both soil and each specific pesticide [36]. Taking into consideration all these factors in soil, what happens with the degradation of different kinds of pesticides in BPS?

Undoubtedly, the factors that govern the movement and degradation process in soil are likely to be similar to those taking place within BPS. For instance, the accelerated degradation observed in soil for some pesticides has also been demonstrated in BPS for compounds such as carbofuran, carbendazim, or metalaxyl [37–39]. Likewise, its composition, as well as the type of substrates present in the organic biomixture, makes BPS a crucial and efficient system for retention and degradation of chemicals [12], compared to soil. Moreover, the presence of lignocellulosic substrates should promote the development and establishment of a robust and active microbiota responsible for the degradation of pesticides. In this regard, a great variety of substrates have been evaluated in BPS biomixtures, for the removal of numerous pesticides. Table 1 summarizes several examples of pesticide degradation from different chemical groups in BPS.

Table 1 Removal of pesticides in selected biomixtures and biopurification systems

Chemical group	Active ingredient	Biomixture evaluated	Concentration evaluated	Main removal results	Reference
Strobilurin	Azoxystrobin	Rice straw – Compost (RS + C) and corn cob – Compost (CC + C)	Two applications of 100 mg L^{-1}	81.5% in RS + C and 68.1% in CC + C	[40]
Neonicotinoid	Imidacloprid	Rice straw – Compost and corn cob – Compost	Two applications of 100 mg L^{-1}	100% in RS + C and CC + C	[40]
Dithiocarbamate	Ethylenebis (dithiocarbamate)	Sugarcane top, banana stem, or eucalyptus chip (at 30%, 50%, or 70% v/v) plus equal parts of sugarcane cachasse and Fluvisol soil	Several applications of 878 mg L^{-1}	The mixtures with 30% sugarcane top (30%) and eucalyptus chip (50%) yielded the best results	[41]
Organophosphate	Chlorpyrifos	Cereal bran, soil and peat (50: 25:25 v/v)	60 mg kg^{-1}	60–70%	[42]
Organophosphate Phenylurea Phenylamide Morpholine	Chlorpyrifos Malathion Linuron Metalaxyl Dimethomorph	Coconut fiber, compost, and soil pre-exposed to pesticides (50:25:25 v/v)	Five applications simulating field conditions between 64–240 mg kg^{-1}	100% metalaxyl and malathion; 20% chlorpyrifos; 10% dimethomorph	[6]
Phosphonoglycine	Glyphosate	Agricultural soil, alfalfa straw/wheat stubble, and river waste; biomixtures were evaluated with and without earthworms addition	1,000 mg kg^{-1}	Between 80% and 90% after 90 days, with or without earthworms, respectively	[43]
Organophosphate	Glyphosate and its metabolite (aminomethyl)-phosphonic acid (AMPA)	Biomixtures containing a mixture of an agricultural soil with alfalfa straw/wheat stubble, as lignocellulosic substrates, and river waste	1,000 mg kg^{-1}	85–99%	[44]
Phenylamide Neonicotinoid	Diuron Imidacloprid	Soil, peat, straw and soil, vermicompost of wet olive	Between 0 and 70 mg kg^{-1}	58–100% diuron; 19–61% imidacloprid; 12–49%	[45]

Triazole Diphenyl ether	Tebuconazole Oxyfluorfen	cake, olive tree pruning (25:25:50 v/v, each)		tebuconazole; 47–74% oxyfluorfen.	
Triazine Triazole Organophosphate Carbamate Benzimidazole	Ametryn Atrazine Cyanazine Cyromazine Prometon Prometryn Simazine Terbuthylazine Bitertanol Cyproconazole Difenoconazole Coumaphos Dichlorvos Dimethoate Malathion Triazophos Carbaril Methiocarb Carbendazim (among others)	Coconut fiber, compost, soil (45:13:42 v/v)	Pesticide mixture containing 10 triazines, 13 triazoles and 20 organophosphates between 4–8 mg kg^{-1} each. -Treatment of real wastewater containing 38 pesticides at varied concentrations	Removal of triazines (59%), organophosphates (68%) and triazoles (failed). For real wastewater, removal of triazines (54%), organophosphates (90%), triazoles (73%), carbamates (71%), other groups (<90%)	[28]
Oxathiin Phenylamide Pyrazole carboxamide Phenylpyrrole Chloronitrile Benzimidazole	Carboxin Metalaxyl-M Fluxapyroxad Fludioxonil Chlorothalonil Thiabendazole	Straw, spent mushroom substrate and soil (25:50:25 v/v)	10, 20, and 150 mg kg^{-1}	Carboxin was the least persistent, followed by metalaxyl-M, while fludioxonil and fluxapyroxad were the most persistent compounds. DT_{50} varied from 2 days to 142 days	[46]
Phenoxyacetic acid Triazine	2,4-dichlorophenoxyacetic acid (2,4-D)	Agricultural soil, sisal pulp, and vegetable compost, corn	1.08, 2.50, 0.23, 0.34, and 0.36 mg mL^{-1} of	>98% for all pesticides after 20 days	[47]

(continued)

Table 1 (continued)

Chemical group	Active ingredient	Biomixture evaluated	Concentration evaluated	Main removal results	Reference
Carbamate Organophosphate Phosphonoglycine	Atrazine Carbofuran Diazinon Glyphosate	stover and seaweed in different proportions (soil accounted for 50% in all biobeds)	biomixture (total pesticide concentration)		
Phosphonoglycines	Glyphosate	Alfalfa straw, wheat stubble, river waste and two different soils	1,000 mg kg^{-1}	88–100%	[48]
Neonicotinoid Organophosphate Triazole Phenylamide Diphenyl ether	Imidacloprid Dimethoate Tebuconazole Diuron Oxyfluorfen	Two biomixtures with soil mixed with pruning and raw wet olive cake or vermicomposted (25:50:25 v/v); one biomixture with soil, straw and peat (25:50:25 v/v).	50 mg kg^{-1} each pesticide	100% dimethoate; 80% imidacloprid; 73% tebuconazole; 75% diuron; 50% oxyfluorfen.	[49]
Phenoxyacetic acid Hydroxybenzonitrile Sulfonylurea Pyrazolone Triazolone Pyrazolium Thiophenes	2,4-D Bromoxynil Thifensulfuron-methyl Tribenuron-methyl Pyrasulfotole Thiencarbazone-methyl Metsulfuron-methyl	Topsoil, composted manure and chopped wheat straw	0.6 mg g^{-1} for all pesticides except for bromoxynil that was 3.36 mg g^{-1}	100% 2,4-D, bromoxynil, and thifensulfuron-methyl, after 35 days; 93% tribenuron-methyl; 70% pyrasulfotole; 64% thiencarbazone-methyl; 34% metsulfuron-methyl	[50]
Phenoxyacetic acid Triazine Carbamate Organophosphate Phosphonoglycines	2,4-D Atrazine Carbofuran Diazinon Glyphosate	11 Biomixtures made of vegetable compost, sisal pulp, corn stover and seaweed	1.08, 2.50, 0.23, 0.34, and 0.36 mg cm^{-3} of biomixture, respectively	>99% for all pesticides	[51]
Carbamate	Carbofuran	Coconut fiber, garden compost and soil pre-exposed to carbofuran (50:25:25 v/v)	20 mg kg^{-1}	9.9% after first application; >88.5% in subsequent applications for 6 months	[52]

Dicarboximide	Iprodione	Soil, wheat straw and peat (25:50:25 v/v)	90.9 mmol kg^{-1} (dw)	DT$_{50}$ between 3.4 days and 4.6 days	[53]
Triazine Organophosphate Dicarboximide	Atrazine Chlorpyrifos Iprodione	Soil, wheat straw and peat (25:50:25 v/v)	35 mg kg^{-1} each	>95% for all pesticides after 5 days	[54]
Triazine	Atrazine	Soil, wheat straw, and peat (25:50:25 v/v) inoculated with immobilized white-rot fungus	80 mg kg^{-1}	78–93%	[55]
Biphenyl Imidazole	Ortho-phenylphenol Imazalil	Spent mushroom substrate of *Pleurotus ostreatus,* either alone or in mixture with straw and soil at (50:25:25 v/v)	4062.5 g m^{-3} and 235.5 g m^{-3} of substrate, respectively	Reduced leaching of pesticides which corresponded to 0.014–1.1% (ortho-phenylphenol) and 0.120–0.420% (imazalil) of their initial concentration	[56]
Triazine Triazole Carboxamide Dinitroaniline	Terbuthylazine Difenoconazole Diflufenican Pendimethalin	Several biomixtures containing substrates such as cork, straw, coat pine and LECA (Light Expanded Clay Aggregates), with and without bioaugmentation with the fungus *Lentinula edodes*	20 mg kg^{-1} difenoconazole and diflufenican; 65 mg kg^{-1} pendimethalin and terbuthylazine	13–76% after 120 days in non-bioaugmented biomixtures; 45–99% in bioaugmented biomixtures	[57]
Carbamate	Carbofuran	Rice husk, compost, and soil biomixture (several compositions) bioaugmented with *Trametes versicolor*	~15 mg kg^{-1}	22–46% after 3 days	[58]

(continued)

Table 1 (continued)

Chemical group	Active ingredient	Biomixture evaluated	Concentration evaluated	Main removal results	Reference
Carbamate	Carbofuran	Five different lignocellulosic materials (sugarcane bagasse, coconut fiber, rice husk, wood chips and newsprint paper) mixed with either compost or peat and soil (50:25:25 v/v)	$30\ \mathrm{mg\ kg^{-1}}$	98.5% after 16 days at best conditions	[59]
Triazine Organophosphate Dicarboximide	Atrazine Chlorpyrifos Iprodione	Soil, wheat straw and peat at (25:50:25 v/v)	$35\ \mathrm{mg\ L^{-1}}$ each added at 0.6 L and 1.2 L of water per day	>95%	[60]
Chloronitrile Neonicotinoid	Chlorothalonil Imidacloprid	Soil, spent mushroom, wheat straw (25:25:50 v/v)	$100\ \mu\mathrm{g\ g^{-1}}$ each	Dissipation rate constant: Chlorothalonil 0.031–0.105, imidacloprid 0.009–0.031	[61]
Triazine	Atrazine	Soil, wheat straw, peat (25:50:25 v/v) amended with rich terpene substrates (5% w/w)	10 and $20\ \mathrm{mg\ kg^{-1}}$	95–98%	[62]

The diversity of chemical structures that can be efficiently treated in BPS is remarkable. As shown in Table 1, several neonicotinoids, dithiocarbamates, organophosphates, phenylureas, acylalanines, triazines, triazoles, nitriles, dicarboximides, carbamates, benzonitriles, and dinitroanilines, among others, have been degraded in BPS to some extent, even reaching a high elimination of over 80%. Despite the high versatility demonstrated by BPS in terms of their removal capacity of diverse compounds, some pesticides have shown little or no degradation in these systems. In this respect, various works have described a high recalcitrance of some insecticide neonicotinoids [63] and fungicide triazoles [64] in soil, even when the microbial degradation of these groups is considered to be the most efficient method for their elimination [64, 65]. Interestingly, the same resistance to degradation has also been observed for several neonicotinoids [27, 66] and triazoles [27, 38, 67] in BPS. The low removal observed for triazoles might be related to their harmful effect as fungicides on ligninolytic fungi developed in the biomixture, since this group of microorganisms is associated with the first steps in some degradation processes within BPS [1].

On the other hand, it is clear that removal of a specific pesticide may vary depending on the biomixture (i.e., materials selection) employed, as well as the operating conditions and even the combination of pesticides treated in the BPS. For example, the combined application of azoxystrobin (strobilurin) and imidacloprid (neonicotinoid) in a BPS composed of rice straw/compost or corn cob/compost biomixtures resulted in an efficient retention of both pesticides, the complete degradation of imidacloprid, and azoxystrobin degradation ranging from 68.1% to 81.5% depending on the biomixture [40]. Interestingly, another study carried out by Kumari et al. [68] revealed that imidacloprid degradation in the same biomixtures was reduced by five- to nine-fold when unconditioned biomixtures were employed (without a previous incubation period); a change that did not affect azoxystrobin removal. Similar studies carried out with the organophosphate chlorpyrifos showed that pre-conditioning of the biomixture (straw, peat, soil, 50:25:25 v/v) did not cause a delay in the degradation processes, reaching values >50% [24]; however, the degradation rate was affected by the concentration of chlorpyrifos applied. Vischetti et al. [33] described the composition of the biomixture as a more determinant factor in chlorpyrifos degradation, where low pH and low C/N ratio favored greater degradation of the compound. Moreover, different composition of biomixtures can lead to the accumulation of 3,5,6-trichloro-2-pyridinol (TCP), the main degradation product of chlorpyrifos; this metabolite exhibits antimicrobial properties that may cause alterations in microbial communities of BPS, thus hindering the degradation of pesticides [17]. Similarly, the production of metabolites with antimicrobial properties, reported for other pesticides in soil [69–71], may affect bacterial composition of BPS, also translating into delays in pesticide degradation.

Modification of biomixture composition results in removal variations. For instance, the degradation of a mixture of imidacloprid, oxyfluorfen, tebuconazole, and diuron in a biomixture composed of straw, peat, and soil (50:25:25 v/v) resulted in complete removal of diuron and partial removal of the remaining compounds (from 45.7% to 55.3%) [45]. When the biomixture was modified by the addition of vermicompost a decrease in the degradation of all pesticides was observed, ranging from 11.8% to 58.8%, including diuron.

Removal of specific pesticides also seems to be dependent on the combination of pesticides simultaneously applied or coexisting in the biomixture. In this respect, higher degradation rates for individual pesticides have been described compared to those achieved when the active ingredients were applied as mixtures in the BPS [46]. Such behavior was observed in a work by Masís-Mora et al. [28], who evaluated the degradation of pesticide mixtures from single chemical families (10 triazines, 13 triazoles, and 20 organophosphates, at 4–8 mg kg^{-1} each), on a biomixture composed of coconut fiber (45%), compost (13%), and farm soil (42%) at laboratory scale. The results showed that organophosphates were degraded at the largest extent (68%), followed by triazines (59%), while the degradation of triazoles failed. The same work also evaluated the degradation of 38 pesticides contained in real wastewater of laboratory origin at low concentrations on a pilot-scale BPS; interestingly, in this case triazoles were degraded at 73%, while triazines, organophosphates, and carbamates were removed at 54%, 90%, and 71%, respectively, showing a delay or an increase in the removal of some pesticides depending on their initial concentrations applied in the BPS.

In this chapter, we made a brief summary of the diversity of pesticides whose removal has been evaluated in BPS. Although we cannot include all structures assayed so far, it is remarkable that BPS exhibit in most cases a higher capacity to remove pesticides than soil. As shown in Table 1, different removal patterns are observed even for the same pesticide depending on factors such as the co-application with other active ingredients or the composition of the biomixture employed, which severely affects degradation kinetics. Hence, it is difficult to draw a general recommendation or a specific biomixture composition for a particular pesticide or mixture of pesticides. In this respect, field conditions must be evaluated depending on each particular situation to select the biomixture that favors the highest pesticide degradation and detoxification in the BPS, and to assay the efficiency of a BPS to remove complex mixtures of pesticides; regarding the latter recommendation, the evaluation of BPS during complete pesticide application cycles of specific crops represents a critical gap in the current knowledge of these systems.

3 Description of Microbial Communities During the Operation of BPS

As mentioned before, soil represents the main source of pesticide-degrading microorganisms and their catabolic gene pool in BPS. In consequence, it is generally accepted that the degradation and mineralization processes in BPS occur broadly in a similar way as they do in soil. For instance, bacteria and fungi represent the dominant organisms in soil regarding biomass and metabolic activity [72] and are considered the main groups with respect to pesticide degradation both in soils [73] and in BPS. Oftentimes, fungi are in charge of transforming pesticides through minor structural changes in the molecule, rendering it non-toxic and susceptible to further degradation by bacteria [74]. It is important to point out that pesticide mineralization in complex natural matrices is often carried out by the combined action of microbial communities and abiotic factors, instead of isolated microbial species only [75]. Nonetheless, only a limited number of studies have described the structure and changes in the microbial communities of BPS upon contaminant influx. This information is important because the composition of the microbial community may strongly influence the efficiency of pesticide degradation.

Earlier works involved the use of phospholipid fatty acid analysis (PLFA) [76] and denaturing gradient gel electrophoresis (DGGE) [52, 77–83], while more recent works utilized quantitative PCR (qPCR) [53, 56] next-generation amplicon sequencing [47, 84–87] and DNA Stable Isotope Probing (DNA-SIP) [88].

Several studies have found little or no effect of pesticide applications on the microbial community when assessed by DGGE. For instance, elimination of atrazine, chlorpyrifos, and iprodione and microbial community changes in biomixture column systems with and without a plant cover were assessed and it was found that presence of rhizosphere enhanced pesticide dissipation, but microbial communities were not affected by the application of the pesticide mixture [80]. A similar study was undertaken at a larger scale with repeated applications of the pesticides reaching similar conclusions [79]. Likewise, it has been observed that repeated atrazine and carbendazim applications had only a minor and transient effect on the microbial community structure of biomixtures composed of straw, peat, and soil [81, 82]. A study investigating repeated applications of carbofuran to a biomixture composed of straw, compost, and soil revealed modest changes on microbial community patterns occurring through time [52]. Similarly, it has been observed that addition of the antibiotic oxytetracycline to a biomixture used to degrade a mix of pesticides (atrazine, carbendazim, carbofuran, and metalaxyl) did not affect the efficiency of pesticide removal or the bacterial and fungal community structure [77].

On the other hand, other studies using similar molecular fingerprinting techniques have revealed more evident changes in the microbial composition of these systems. Fungicide dissipation and microbial changes were assessed in a biomixture composed of pruning residues and straw. Both penconazole and fludioxonil generated a notorious change in the microbial community, mainly attributed to inhibition of the fungal fraction by these compounds, however these effects were transitory [76]. Another study also investigating the effect of fungicides in a similar matrix showed changes in the microbial community through DGGE analysis, but likewise, the modification was only temporary [78]. An additional study employed pilot-scale biofilters that were treated with chlorpropham and found that community diversity significantly increased over time [83].

In general, when assessed by molecular fingerprinting techniques such as DGGE, a moderate modification of the overall community structure with the addition of some pesticides can be observed, while for others, the effects appear to be very limited.

Techniques capable of targeting specific microbial groups, such as qPCR, have also been used to evaluate the abundance of microbial populations of interest in BPS systems. For instance, an increased abundance of total bacteria and fungi was observed in pilot-scale BPS exposed to high levels of pesticides in simulated effluents from fruit packaging plants. It was found that the community was dominated by Actinobacteria, Firmicutes, and α-Proteobacteria [56]. In another study, bioaugmentation and rhizosphere assisted biodegradation were successfully used to maximize the dissipation of iprodione in BPS packing material. qPCR showed that changes in the abundance of α-Proteobacteria and Firmicutes were driven by the presence of rhizosphere while bioaugmentation had no significant effect in this respect [53]. This technique is suitable when targeted evaluation of microbial populations is required.

Molecular techniques capable of simultaneously targeting a broad range of known and unknown organisms, such as next generation sequencing, have added to the body of information and have increased our understanding of the microbial changes during pesticide addition and dissipation in BPS [2]. Pyrosequencing, in this case combined with DGGE, was used to study an operational BPS exposed to a variety of pesticides. Significant community changes were detected, most notably, a decrease in community diversity. Also, certain groups such as Gammaproteobacteria showed an increased relative abundance, while a decrease of Firmicutes and Bacteroidetes was observed [87]. Illumina amplicon sequencing was used to study the variations in bacterial and fungal communities within BPS exposed to different pesticide rinsates. It was found that exposure to pesticides generated an increase in bacterial diversity, while the effect on fungal diversity was variable [85]. The same method was used to assess microbial diversity in miniature biobed systems with different kinds of biomixture exposed to atrazine, carbofuran, diazinon, glyphosate, and 2,4-D. The type of biomixture had a significant effect on diversity in all biomixtures. Additionally, diversity had an important effect on the residual amount of pesticides at the end of the assay [47]. Oxford Nanopore sequencing of amplicons has also been used to characterize the microbial population of a biomixture obtained from an operational BPS repeatedly exposed to a mixture of pesticides, including chlorpyrifos and iprodione. It was found that the microbial community composition was mainly formed by the phyla Proteobacteria, Firmicutes, Bacteroidetes, and Actinobacteria [86].

Finally, DNA-SIP has been used as a culture-independent approach to identify microorganisms of the genera *Ramlibacter*, *Variovorax,* and an unknown genus of the family Comamonadaceae as the dominant linuron degraders in a biomixture. *Ramlibacter* could not be isolated by selective enrichment from the matrix. This study highlights the biases that cultivation techniques introduce when used to identify pesticide-degrading microorganisms [88].

These newer, more informative techniques will provide further knowledge on the dynamics of microbial communities within biomixtures. Gathering this information potentially represents a key step to improve the performance of BPS. Furthermore, the identification of the most important degrading communities would provide more targeted inputs for biostimulation/bioaugmentation of BPS.

4 Alternative Applications: Effects of Antibiotics of Agricultural Use During Co-Disposal in BPS

The application of agrochemicals in agricultural activities is not restricted to pesticides; plant growth regulators (promoters or retardants), fertilizers, and other crop protection chemicals such as antibiotics also make up the diversity of compounds employed in this industry [89]. Considering that most antibiotic application strategies employed in agriculture resemble those used for pesticide application, on-farm production of antibiotic-containing wastewater is also a consequence of pest management.

Antibiotics used in agriculture are restricted to a small number of molecules, in contrast to what happens in human and veterinary medicine. Currently, only two drugs, oxytetracycline and streptomycin, are registered by the EPA for use in plant agriculture [90]. However, other antimicrobials including gentamicin, oxolinic acid [91], kasugamycin, and validamycin [92] are also used in several geographical regions for the same purpose.

The release of wastewater containing high loads of antibiotics represents an important environmental risk, which is why they should be treated to avoid antibiotic exposure to ecosystems. Due to their action over non-target organisms, the release of antibiotics in the environment may exert adverse effects on diverse natural and anthropogenic-related processes, such as nitrification and iron reduction in aquatic systems [93, 94], enzymatic activity in soils [95], sulfate reduction and decomposition of organic matter in wastewater treatment plants [96], anaerobic digestion and biogas production [97, 98], and the Anammox process [99]. In addition, the potential spread of antibiotic-resistance genes has also been linked to environmental exposure to antibiotics [100], a problem that is partially solved by the use of different antibiotics, at least in animal/human medicine.

For these reasons, the use of BPS for the disposal and treatment of antibiotic-containing wastewater has been considered as a novel application of such systems. However, the mechanism of action of antibiotics would apparently stand as the main disadvantage against this use, as their bactericidal or bacteriostatic action might result in the inhibition of microbial communities and subsequently in the removal capacity of BPS. It is true that some deleterious effects of antibiotics are reported only at concentrations usually higher than those detected in real environmental samples; however, considering the nature of agricultural wastewater and their corresponding disposal, these high concentrations could be reached within BPS.

Most of the studies conducted so far on the effect of antibiotics during co-disposal of pesticides contradict the hypothesis of inhibition in the efficiency of pesticide degradation in BPS. Such effects have been evaluated in the mineralization and removal of several pesticides, when different doses of oxytetracycline, kasugamycin, or the commercial formulation of oxytetracycline+gentamicin were simultaneously applied to functional biomixtures.

A pesticide mineralization process indicates that the agrochemical is completely oxidized to yield inorganic compounds (CO_2 and H_2O under aerobic conditions), thus preventing the accumulation of organic transformation products of potential toxicity in the BPS. Pesticide mineralization analyses are usually based on the use of ^{14}C-radiolabeled pesticides, whose mineralization yields $^{14}CO_2$ that can be easily distinguished from the CO_2 produced in the biomixture through the metabolization of other sources (respiration of other substrates in the matrix) [101]. The effect of antibiotics on the mineralization of pesticides has been analyzed in biomixtures, mainly employing ^{14}C-chlorpyrifos and ^{14}C-carbofuran as model pesticides (Table 2).

The co-application of a commercial formulation of oxytetracycline resulted in the stimulation of ^{14}C-chlorpyrifos mineralization rates at low doses of 0.1 and 1 mg kg^{-1}; on the contrary, high antibiotic doses of 100, 500, and 1,000 mg kg^{-1} caused an important decrease in mineralization rates [102]; the dose of 10 mg kg^{-1}, the one more likely to occur within BPS biomixtures, seemed to affect this parameter the least. This pattern has been described as a hormetic-like response to the antibiotic, in which low, non-inhibitory concentrations enhance certain metabolic activities of microbial communities, while higher, inhibitory doses, evolve into their depression [105]. An analogous hormetic-like response was also observed during the co-application of the same oxytetracycline formulation during ^{14}C-carbofuran removal in biomixtures [39]; however, in that case, stimulation in the mineralization rate was observed at concentrations ranging from 0.1 mg kg^{-1} to as high as 500 mg kg^{-1}, and only the extreme dose of 1,000 mg kg^{-1} delayed mineralization.

The co-application of kasugamycin also produced stimulation in the mineralization of ^{14}C-chlorpyrifos; in particular, the mineralization rate also exhibited a hormetic-like response, with markedly increased rates at concentrations ranging from 0.1 to 100 mg kg^{-1}, and a deleterious effect only at the dose of 1,000 mg kg^{-1} [37]. The stimulation of the process was remarkably higher than that achieved with oxytetracycline, reaching a value of more than 250% in the parameter of mineralization rate at a dose of 0.1 mg kg^{-1}, with respect to the system without antibiotics. Curiously, the maximum mineralization estimated was higher for each of the tested antibiotic doses, even those that decreased the mineralization rate.

A different panorama has been observed when the commercial formulation of oxytetracycline+gentamicin was co-applied with ^{14}C-chlorpyrifos, resulting in an important decrease of mineralization rates, from 15 to 50%, at every dose tested [37]. Despite reducing the speed of mineralization, most doses, on the contrary, produced an increase in the maximum estimated mineralization, thus not discouraging at all the potential co-disposal of this formulation with pesticides in BPS.

The observations achieved with oxytetracycline and kasugamycin formulations revealed an enhancement in the removal of recalcitrant pesticides; moreover, they indicate that BPS might be used for the co-disposal of pesticides and antibiotics, without necessarily jeopardizing the pesticide removal capacity of the system. The fact that potential antibiotic concentrations in BPS (5–50 mg kg^{-1}) fall within those for which mineralization enhancement has been achieved supports the relevance of this practice. Nonetheless, the pattern observed for ^{14}C-chlorpyrifos and ^{14}C-carbofuran cannot be generalized, and the response of other pesticides should be evaluated, as well as the effect of other antibiotic formulations.

Table 2 Effect of co-disposal of antibiotics on the removal of pesticides in biopurification systems

Pesticide	Chemical group/ function	Process assayed (mineralization/removal)	Co-disposed antibiotic	Effect on pesticide elimination	Reference
Ametryn	Triazine/herbicide	Removal	Oxytetracycline	Ranged from no alteration to duplication of DT_{50}	[27, 102, 103]
Atrazine	Triazine/herbicide	Removal	Oxytetracycline	No effect regardless of the mixture of pesticides treated in the BPS	[27, 77, 102, 104]
Carbendazim	Benzimidazole/ fungicide	Removal	Oxytetracycline	Ranged from no alteration to increase (three-fold) of DT_{50} depending on the mixture of pesticides treated in the BPS	[27, 77, 104]
			Kasugamycin	No alteration	[37]
			Oxytetracycline +Gentamicin	No alteration	
Carbofuran	Carbamate/insecticide-nematicide	Mineralization	Oxytetracycline	Hormetic-like effect in mineralization rate: increase at low-high doses (0,1 to 500 mg kg^{-1}), decrease at very high doses (1,000 mg kg^{-1})	[39, 77, 104]
		Removal	Oxytetracycline	No alteration	
Chlorpyrifos	Organophosphate/ insecticide	Mineralization	Kasugamycin	Hormetic-like effect in mineralization rate: increase at low-medium doses (0.1, 1, 10, 100 mg kg^{-1}), decrease at high doses (1,000 mg kg^{-1}). Increase in maximum mineralization at every dose.	[37, 102]
			Oxytetracycline	Hormetic-like effect in mineralization rate and maximum mineralization: increase at low doses (0.1 and 1 mg kg^{-1}), no apparent effect at medium dose (10 mg kg^{-1}), decrease at high doses (100, 500, 1,000 mg kg^{-1})	
			Oxytetracycline +Gentamicin	Decrease in mineralization rate at every dose (0.1 to 1,000 mg kg^{-1}). Increase in maximum mineralization value at most doses	

(continued)

Table 2 (continued)

Pesticide	Chemical group/ function	Process assayed (mineralization/removal)	Co-disposed antibiotic	Effect on pesticide elimination	Reference
Metalaxyl	Phenylamide/ fungicide	Removal	Oxytetracycline	Ranged from no alteration to increase (1.5 to 2.7-fold) of DT_{50} depending on the mixture of pesticides treated in the BPS	[27, 77, 104]
			Kasugamycin	No alteration	[37]
			Oxytetracycline +Gentamicin	No alteration	
Linuron	Urea/herbicide	Removal	Oxytetracycline	Ranged from no alteration to slight increase (1.3-fold) of DT_{50} depending on the mixture of pesticides treated in the BPS	[27, 102]
Terbutryn	Triazine/herbicide	Removal	Oxytetracycline	Slight decrease (0.67-fold) of DT_{50}	[103]

A different scenario has been observed for pesticide removal (instead of mineralization) in BPS during co-application of antibiotics: the process mostly ranges from no significant alteration to delays in the removal, revealed as an increase in the half-life (DT_{50}) values for some pesticides, depending on specific conditions (Table 2). That said, contrary to mineralization, enhancement or stimulation has not been described as a common feature in the removal of pesticides in the presence of antibiotics (with some exceptions, as indicated below). The following discussion refers to observations obtained using potential antibiotic concentrations in BPS (from 10 to 40 mg kg^{-1}), according to real application practices.

The removal of several herbicides belonging to the group of triazines has revealed different patterns when co-applied with oxytetracycline. There seems to be no alteration on atrazine removal, as DT_{50} values have not significantly differed from control biomixtures without the antibiotic; this pattern has been the same regardless of the mixture of pesticides treated, ranging from just a few herbicides to complex mixtures of up to nine active ingredients [27, 77, 102, 104]. On the contrary, ametryn removal showed no significant alteration in a biomixture simultaneously treating nine pesticides (three herbicides, two fungicides, and two insecticides) [27], while its DT_{50} was doubled (from 43.9 days to 92.4 days) in a simpler mixture containing only the herbicides [102]. A marginal enhancement in the removal of triazines was also described by Cambronero-Heinrichs et al. [103] in the cases of ametryn (DT_{50} decreased from 34.8 days to 28.4 days) and terbutryn (DT_{50} decreased from 51.0 days to 34.0 days), during their simultaneous removal in biomixtures containing oxytetracycline. Some differences might also be ascribed to the heterogeneity in microbial communities from one biomixture to another, depending on the origin of the soil and other materials employed in their production.

Removal of linuron, a phenylurea herbicide, followed a pattern that resembled that from ametryn during co-application of oxytetracycline: no alteration during the elimination of a complex mixture of pesticides [27], and some delay (DT_{50} increased from 30.7 days to 40.1 days) only in the removal of three herbicides [102]. Interestingly, such delays observed in the case of herbicides do not affect final removal values.

The effect of oxytetracycline was also assayed during the elimination of the insecticide carbofuran, whose removal was not affected even by successive co-applications of the antibiotic (every 7 days; four applications) at relevant BPS concentrations [39]. Moreover, a second dose of carbofuran applied 14 days after the first one revealed accelerated degradation of this compound, a process that also was not inhibited by the antibiotic. Furthermore, no alteration was demonstrated during the elimination of carbofuran in biomixtures used for the simultaneous elimination of other pesticides [77, 104]; nor during the removal of its transformation products [39].

The effect on the removal of the fungicides carbendazim and metalaxyl was evaluated with several antibiotics of agricultural use. First, when oxytetracycline was co-applied in a biomixture for the elimination of six pesticides (four fungicides plus two insecticides), the removal of both fungicides was delayed: DT_{50} increased from 8.9 days to 26.8 days for carbendazim, and from 6.5 days to 17.5 days for metalaxyl [27]. Then, during the elimination of nine pesticides (the latter plus three insecticides), no delay was observed for carbendazim due to oxytetracycline (although the DT_{50} was significantly higher in the absence of the antibiotic), while a lower delay was still observed for metalaxyl (DT_{50} increased from 8.8 days to 12.9 days). On the contrary, no alterations were recorded in the DT_{50} values for both fungicides when the effect was assayed with the commercial formulations of kasugamycin or oxytetracycline+gentamicin [37]. However, in this case the biomixture had been previously exposed to carbendazim and metalaxyl, and accelerated degradation was achieved for both fungicides (observed as much lower DT_{50} values); such effect could have masked potential effects due to antibiotics after first pesticide/antibiotic application, as most reports describe. Conversely, these findings further support the evidence for co-disposing antibiotics and pesticides in the same BPS, without significant depletion of its removal capacity.

The rationale behind disposing antibiotic-containing wastewater in BPS is aiming to achieve antibiotic removal, as in the case of pesticides. In this respect, current evidence reveals that oxytetracycline is actually removed in biomixtures. Jiménez-Gamboa et al. [39] and Cambronero-Heinrichs et al. [103] reported DT_{50} values of 34 days and 38 days, respectively, which are shorter than those described in soil [106] and in some anaerobic systems [97, 107], although they are similar or longer than values achieved in matrices containing manure [106, 108]. More research is necessary to enhance oxytetracycline removal in BPS; moreover, the dissipation of other agricultural antibiotics such as kasugamycin or gentamicin is yet to be evaluated in BPS.

Even though elimination delays have been described for some pesticides, the removal capacity of BPS is not significantly hindered in the presence of relevant antibiotic concentrations. On the contrary, the enhancement of processes such as mineralization supports the practice of co-disposal of antibiotics and pesticides in the same BPS, thus resulting in lower operational costs and smaller areas devoted for BPS within agricultural fields. As DT_{50} values for pesticide elimination depend not only on the co-application of antibiotics, but also on the mixture of pesticides disposed in a specific BPS, effects and removal performance (including antibiotic removal) should be assayed for each specific case of pesticide application cycle for a given crop.

5 Alternative Applications: Use of BPS for the Removal of Pharmaceuticals

Despite being typically employed for the removal of pesticides, or more recently for the elimination of antibiotics of agricultural use from wastewater of agricultural origin, the application of BPS for the removal of pharmaceutical-containing effluents has been recently under exploration. This incipient approach clearly depends on how feasible a BPS configuration can be adapted to treat the high volume of effluents usually polluted with pharmaceuticals. Hence, the studies here discussed employed small biomixture systems, of up to a few kilograms.

Delgado-Moreno et al. [49] described the use of biomixtures containing soil and raw olive mill cake or its vermicompost for the removal of diclofenac, ibuprofen, and triclosan from wastewater. Removal values over 94% were achieved over a period of 84 days in the best scenario, and biodegradation of triclosan and diclofenac was determined to be controlled by their bioaccessible fraction in the system. One of the main advantages of the biomixtures evaluated was their higher adsorption efficiency (compared to soil), which might avoid pollutant transport to other compartments. A similar assay demonstrated slower dissipation of these pharmaceuticals when they were simultaneously applied in the biomixture, and differential alteration in the composition and relative abundance of bacterial taxa, depending on the pharmaceutical [84]. The bioaugmentation of a BPS with an ibuprofen-degrading bacterial strain of *Sphingopyxis granuli* successfully enhanced the degradation of this pharmaceutical even after successive weekly applications, increasing dissipation rates by up to three-fold in the biomixture, and reducing the accumulation of transformation products [109]. Bioaugmentation of the BPS with aqueous extracts from a previously acclimated biomixture (exposed to the same compounds) at least partially improved the dissipation of the pharmaceuticals [110].

Similarly, other biomixture-like matrices composed of wheat straw pellets (lignocellulosic substrate) mixed with sewage sludge naturally contaminated with pharmaceuticals were successfully employed for the removal of several compounds, including atorvastatin, clarithromycin, fenofibrate, hydrochlorothiazide, ibuprofen, and ranitidine [111]. Such mixtures have commonly been evaluated as bioaugmented matrices, particularly with the ligninolytic fungus *Trametes versicolor*; this approach has achieved efficient elimination of diverse pharmaceuticals (the previously mentioned plus atenolol, bezafibrate, cimetidine, diclofenac, mefenamic acid, naproxen, sulfamethazine, among others) but lower elimination of psychiatric drugs like diazepam and carbamazepine [111–113]. Analogous to traditional biomixtures aimed at pesticide removal, this approach (bioaugmentation aside) also relies on the presence of pharmaceutical microbial degrading communities within the contaminated matrix (i.e. sewage sludge), which is pre-exposed to these compounds.

The treatment of effluents, either wastewater or sludge, still requires further optimization, and in particular, proper approaches to scale up the process, considering that such effluents are of higher flow/volume than those containing pesticides produced at farm level.

6 Challenges and Future Prospects

Research on BPS has been mostly performed in Europe and Latin America, and despite a few exceptions in European countries (and Guatemala in Latin America), extensive application has not been reached yet. The lack of legislation regarding the treatment of pesticide residues, as well as the explicit inclusion of BPS as a treatment option, represents one of the biggest challenges to achieve the generalized implementation of the BPS technology. Contrary to those few European countries where BPS are included in local legislation, gaps in their Latin American counterparts limit their extensive application. Another challenge for a more generalized utilization of this technology is the delivery of adequate training to the farmers, particularly in less developed countries, especially because they might not have been exposed to enough information regarding the use and advantages of BPS.

Further research on the evaluation of real pesticide application cycles to assay the potential accumulation of the most recalcitrant compounds is necessary to properly establish whether single or multiple BPS are required in farms where intensive agricultural activities are undertaken. Furthermore, it is important to assess the removal of different pesticide mixtures, as this represents the real scenario during agricultural production, and mixture complexity may modulate removal performance. In this respect, additional efforts should be targeted at demonstrating detoxification or mineralization of the compounds within the system, and not only their removal or transformation.

Given that only scarce reports describe the long-term efficiency of BPS [52], the useful life of these systems is yet to be determined. Similarly, since no formal studies regarding the disposal of aged biomixtures have been reported, more research should focus on the evaluation of composting, the widely recommended approach, or alternative strategies for BPS discarding; moreover, the disposal of BPS should follow a strict ecotoxicological monitoring of the biomixture waste, to minimize the potential environmental risk.

Experimental evidence suggests that a single BPS could be used for the simultaneous removal of antibiotics and pesticides, thus resulting in lower operational costs and smaller areas devoted for BPS within agricultural fields. Nonetheless, as there is no single golden recipe for biomixture composition, the removal performance should be evaluated for each desired combination of agrochemicals aimed to be degraded in the BPS. Newer, more informative microbial community analysis technologies have started to increase our understanding of the dynamics of degrading communities and will provide novel insights on their identification, selection of the most suitable specialized strains, and identification and monitoring of specific degrading genes. This information will prove vital for the enhancement of BPS performance in the near future.

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Abiotic and Biological Technologies for the Remediation of Phenylurea Herbicides in Soils

Alba Lara-Moreno, Jaime Villaverde, Marina Rubio-Bellido, Fernando Madrid, and Esmeralda Morillo

Contents

Abstract Phenylurea herbicides (PUHs) are reported to be amongst the most extensively used herbicides in agriculture for pre- and post-emergence control of weeds and mosses in a wide variety of crops. Most of the PUHs have been forbidden in some European countries due to their presence in water and soil, which leads to serious environmental and public health problems in a wide variety of organisms, including humans. This review gives an overview of abiotic and biological technologies used for the remediation of soils contaminated by PUHs, including their limitations and advantages. PUHs present from low to moderate adsorption to soils, the organic matter content being the main influencing factor. For this reason, the majority of the remediation studies in soils are based on the most hydrophobic PUHs, diuron and linuron. The degradation of PUHs in the environment is primarily considered to be due to microbial transformation, and most of the techniques developed for soils are based on bioremediation, which can be enhanced through biostimulation and bioaugmentation processes, and also by the addition of

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solubilizing agents to increase PUHs bioavailability. But also, abiotic processes have to be considered, remarkable are those that are based on advanced oxidation processes (AOPs), widely used in the decontamination of PUHs in water, but which can be considered as emerging technologies for soils tested only at lab scale.

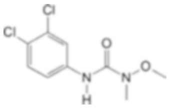
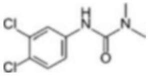
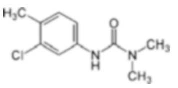
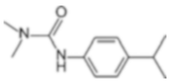
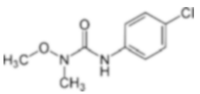
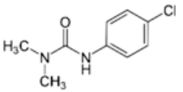
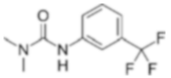
Keywords Bioavailability, Phenylurea herbicides, Remediation technologies, Soil contamination

1 Introduction

Environmental pollution by pesticides is a major problem with wide ecological consequences. The contamination of soil and water (drinking water, wastewaters, and natural waters) by pesticides from agricultural activities has increased significantly [1], and it is responsible for many ecological and health problems [2]. Phenylurea herbicides (PUHs) are amongst the most extensively used herbicides in agriculture worldwide. They are used for pre- and post-emergence control of weeds and mosses in crops (cereals, asparagus, citrus, cotton, or bush fruits) and in non-cropped areas (railway lines, garden paths, roads) [3, 4]. They are systemic herbicides that kill the weeds by inhibition of the photosynthesis resulting in necrosis and chlorosis [5].

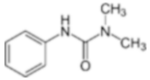
More than 20 PUHs are used for plant control (anisuron, chlorbromuron, chlortoluron, chloroxuron, difenoxuron, dimefuron, diuron, fenuron, fluometuron, isoproturon, linuron, metobromuron, metoxuron, monolinuron, monuron, neburon, phenobenzuron, siduron, tetrafluron, thidiazuron, and some others less well-known), diuron and linuron being the most commonly used and studied. They have a general structure of phenyl–NH–(C=O)–NR2, with one of the urea-N joined to a phenyl group. Both the phenyl group and the free urea-N can be attached to different chemical substitutions, such as methyl, fluoride or chloride groups, and other moieties, which give rise to the different PUHs, as shown in Table 1. Chlortoluron, diuron, linuron, monolinuron, and monuron have one or two chloride groups in the phenyl ring, but at different positions. Fluometuron presents three fluoride groups in its structure, and isoproturon presents an isopropyl group associated with the phenyl ring. Most of the commonly used PUHs are N,N-dimethyl substituted (fenuron, monuron, diuron, chlortoluron, fluometuron, isoproturon) or N-methoxy-N-methyl substituted (e.g. linuron, monolinuron).

Table 1 Formulas, molecular structures and some properties of selected phenylurea herbicides (PPDB. IUPAC Pesticides Properties Database)

Name	IUPAC name	Structural formula	Solubility (mg L^{-1})	Log K_{ow}	K_{oc}	Soil mobility/GUS index[a]	Soil degradation DT_{50}[b]
Linuron	3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea		63.8	3.0	843	Slightly mobile 2.11	48/57.6 Moderately persistent
Diuron	3-(3,4-dichlorophenyl)-1,1-dimethylurea		35.6	2.87	680	Slightly mobile 2.65	146.6/229 Persistent
Chlorotoluron	3-(3-chloro-p-tolyl)-1,1-dimethylurea		74	2.5	196	Moderately mobile	–
Isoproturon	3-(4-isopropylphenyl)-1,1-dimethylurea		70.2	2.5	122[c]	Moderately mobile 2.61	12/23 Non-persistent
Monolinuron	3-(4-chlorophenyl)-1-methoxy-1-methylurea		735	2.2	200	Moderately mobile 2.89	60/– Moderately persistent
Monuron	3-(4-chlorophenyl)-1,1-dimethylurea		230	1.79	150	Moderately mobile 4.07	170/– Persistent
Fluometuron	1,1-dimethyl-3-(α,α,α-trifluoro-m-tolyl)urea		111	2.28	67.4[c]	Mobile 4.24	63.6/89.8 Moderately persistent

(continued)

Table 1 (continued)

Name	IUPAC name	Structural formula	Solubility (mg L^{-1})	Log K_{ow}	K_{oc}	Soil mobility/GUS index[a]	Soil degradation DT_{50}[b]
Fenuron	1,1-dimethyl-3-phenylurea		3,850	0.98	42	Mobile 4.23	60/– Moderately persistent

[a] GUS index indicates the potential to move toward groundwater

[b] DT_{50}, estimated average half-life in soil (lab at 20°C/field)

[c] Kf_{OC} values

2 Behavior of Phenylurea Herbicides in Soil

Some properties of PUHs, such as hydrophobicity or water solubility, are commonly used to predict their environmental fate. PUHs generally have moderate to relatively high solubility in water (Table 1) and, therefore, from low to moderate adsorption to soil based on their octanol-water partition coefficient, Kow [6]. It makes them mobile in soils and irrigation and rainfall can deliver them through leaching and runoff to rivers, groundwater, seawater, and lakes [7, 8]. Water contamination by pesticides due to runoff or leaching is mainly ruled by soil sorption processes, which are governed by both soil and pesticide properties [9, 10].

In relation to soil properties, the sorption of those pesticides that are hydrophobic is highly correlated with soil organic matter (OM) content, but OM is not the only component governing the adsorption of pesticides onto the soil. In the case of PUHs, the OM content is also considered the main soil property that influences their potential adsorption capacity [11–13]. However, Inoue et al. [14] observed that diuron sorption correlated also with the clay content of the soils, and Carbo et al. [15] concluded that clay minerals and the surfaces of Fe and Al amorphous sesquioxides were also responsible. When hydrophobic interactions are the main characteristics responsible for the adsorption of a particular herbicide, Koc values are in a similar range for the different soils studied, but Rubio-Bellido et al. [16] observed that this did not occur in the adsorption of diuron in some soils, concluding that the main variables on diuron adsorption were OM, clay fraction and aluminium oxide surfaces. More recently, Agbaogun and Fischer [17] deduced from correlation analysis that not only OM of soils, which is the most important, but also soil mineral fractions (amorphous Fe and Mn oxides and clay/silt) and CEC were important parameters for PUHs sorption by tropical soils. Ghafoor et al. [18] observed that when soil OM content was $<2\%$, iron and aluminium oxides as well as clay minerals are also important for an accurate prediction of isoproturon sorption.

Besides soil characteristics, the properties presented by PUHs significantly affect the possibility of their adsorption in soils, and, consequently, their mobility and their possibility of reaching water environments. Blondel et al. [19] and Agbaogun and Fischer [17] studied phenylurea molecular properties that affect their adsorption coefficients (Kf, Kd) on soils. They observed that log Kow showed a very strong correlation with Kf and Kd, being higher as higher is the number of chlorine atoms on the phenyl group. The highly electronegative chlorine atom withdraws significant electron charge density from carbon–carbon bonds in the ring structure, exacerbating the hydrophobic effect. Consequently, diuron and linuron, with two chlorine atoms (Table 1), presented the highest log Kow values and, therefore, the highest adsorption to soils. For this reason, both are considered as only slightly mobile, and most of the remediation studies of PUHs in soil are based on diuron and linuron. The presence of a methyl group in diuron and a methoxy group in linuron gives the differences in their Kow values and adsorption coefficients, conferring higher adsorption for linuron. An increase in additional aryl substitutions or n-aliphatic chain length in PUHs leads to higher soil adsorption.

In the same way, those PUHs which are classified as "moderately mobile" (such as chlortoluron, isoproturon, monolinuron, and monuron) or as "mobile" (such as fluometuron, and fenuron) are less frequently detected in soils and more frequently in water environments. Herrero-Hernández et al. [20] and Papadakis et al. [21] observed that fluometuron was among the most frequently detected herbicides in ground and surface waters close to agricultural areas. Fenuron, fluometuron, and their metabolites were found to be stable to aqueous photolysis and hydrolysis, leading to a higher persistence in the environment.

Some of the PUH metabolites which are toxic have also been detected in waters (3,4-dichloroaniline, 3,4-DCA; N-(3,4-dichlorophenyl)urea, DCPU; N-(3,4-dichlorophenyl)-N-methylurea, DCPMU) [22, 23], where they, together with their parent compounds, can lead to serious environmental problems due to their toxic effects on aquatic organisms [24, 25], and vertebrates [26, 27], including humans [28, 29]. For these reasons, many PUHs have been forbidden in European countries. According to the IUPAC Pesticides Properties Database [30], the use of fenuron, monolinuron, and monuron is banned in EU-27 member states; diuron, fluometuron, and isoproturon are permitted in only one, three, and five countries of the EU-27, respectively. However, chlortoluron and linuron are still permitted in 19 and 24 countries of the EU-27, respectively. Moreover, the European Commission [31] has established in the field of water policy, the priority substances for European freshwater resources, under the Water Framework Directive 2013/39/EU. This list contains 45 substances, many of which are pesticides, including the PUHs diuron and isoproturon. Based on such directives, member states have to progressively reduce the release and emission of these substances.

3 Technologies for Remediation of Phenylurea Herbicides

Although dependent on soil type, in general, the natural degradation of PUHs can be relatively slow in the soil. The estimated average half-life (DT50) of these herbicides in soil under laboratory conditions at 20°C and under field conditions is shown in Table 1. As can be observed, the sequence of soil mobility and that of soil degradation of these herbicides are not always coincident. The availability of pollutants for biological and chemical degradation in soils is determined by sorption phenomena, but the facility of PUHs molecules to be degraded also plays an important role. According to the IUPAC Pesticides Properties Database [30], the most persistent PUHs in soils are diuron and monuron. The degradation of PUHs in the environment is primarily due to microbial degradation, and therefore, the majority of the techniques developed to degrade these herbicides in soils are based on bioremediation (the use of living organisms to remediate polluted environments). However, abiotic processes also have to be considered to degrade PUHs, but to a lesser extent [5]. The aim in both types of techniques is to reach the mineralization of these herbicides to CO_2, water and inorganics, or to degrade them into less toxic products.

3.1 Abiotic Remediation

Natural hydrolysis of PUHs in the soil and water, which is a very slow process, produces 3,4-dichloroaniline (3,4-DCA) as a toxic metabolite [3, 23]. Also, chemical oxidation of PUHs has been studied, especially in water, using the traditional oxidizing agents, such as hydrogen peroxide, ozone, chlorine, chlorine dioxide or hypochlorites [32–36]. Unfortunately, several toxic and carcinogenic by-products are generated also during these oxidation processes [37]. Chen and Young [38] observed that diuron was degraded to N-nitrosodimethylamine (NDMA), a human carcinogen, during chlorination. Furthermore, many studies have reported a high diuron removal ratio (>99%) during ozonation. Benitez et al. [39] and Solis et al. [40] observed that single and photocatalytic ozonation led to the complete degradation of all by-products. On the contrary, Wang et al. [41] observed that the metabolite NDMA was formed from some PUHs during ozonation and chloramination, the removal ratios being correlated with the numbers of halogen atoms in the herbicide molecules (isoproturon (0) > chlortoluron (1 Cl) > diuron (2 Cl) > fluometuron (3 F)), and the efficiency of oxidants was: $O_3 > ClO_2 > Cl_2$. The intermediates produced during ozonation of the four herbicides facilitated NDMA production, and also for chlortoluron and isoproturon during ClO_2 oxidation.

In the last two decades, techniques based on advanced oxidation processes (AOPs) have been developed to get a more complete chemical degradation of biorefractory and toxic organic pollutants. The traditional oxidizing agents frequently used are not good enough to degrade certain organic pollutants and their metabolites, but they can combine with iron salts, ultraviolet-visible light irradiation or semiconductors (such as TiO_2, ZnO, CuO, CdS, GaP, or NiO) to improve the degradation results. AOPs techniques present advantages and they are usually carried out at ambient temperature and pressure. They do not produce big amounts of hazardous residues, being considered environmentally friendly [42]. In almost all AOPs, the generation of reactive hydroxyl radicals (•OH, one of the most reactive species) takes place, initiating multiple oxidation reactions that lead to the mineralization of the pollutants [43]. There are various processes to generate •OH radicals, and in the case of PUHs the most commonly used processes are photocatalysis by colloidal particles (TiO_2, ZnO, and CuO), photolysis of hydrogen peroxide, Fenton, photo-Fenton and electro-Fenton oxidations, although oxidation based on ozonation and persulfate oxidants have to also be taken into account. The study and application of these techniques in an aqueous medium are relatively extensive [44, 45], but they are very scarce in soils.

3.1.1 Abiotic Degradation in Water

After microbial degradation of PUHs, photochemical processes are considered to probably be the second cause of their removal in the environment, although to a much lesser degree. Photodegradation of PUHs has been extensively studied in waters due to their presence in wastewater plants [4, 46, 47]. Direct photodegradation leads to partial degradation, and sometimes the metabolites formed may be more toxic for non-target organisms and more persistent than the initial herbicides. For this reason, the direct photolysis of these herbicides has been frequently studied in the absence and presence of different catalysts (photocatalysis). Also for the treatment of polluted water by PUHs, advanced oxidation processes (AOPs) have been proposed, such as heterogeneous photocatalysis, homogeneous photo-Fenton, H2O2/UV, O3/UV or H2O2/O3/UV [48].

Heterogeneous photocatalysis, based on the irradiation of semiconductor particles (TiO2, ZnO, CuO, etc.) suspended in aqueous solutions, usually supported on a porous substrate, is under research for the degradation of PUHs in water due to their simplicity and reusability [36, 49–59]. The semiconductor, upon irradiation with light, induces oxidation and reduction reactions on or close to its surface, the selection of the most suitable substrate being critical.

Due to the variety of photochemical parameters relative to PUHs in water available in the literature, Fabbri et al. [60] modelled the phototransformation kinetics of five PUHs (diuron, isoproturon, chlortoluron, metoxuron, and fenuron) in surface waters. They concluded that the direct photolysis of fenuron was negligible, important for chlortoluron, and somewhat significant for the other compounds (the least photochemically persistent metoxuron and isoproturon, and diuron the most persistent). They also observed that photoreaction pathway was enhanced at intermediate values of dissolved organic carbon (DOC) (1–4 mg L^{-1}), as supported for the photodegradation of other pesticides [61]. Reactions with •HO and excited chromophoric dissolved organic matter (CDOM*) were the main phototransformation pathways, but the reaction between phenylureas and •HO produced more toxic intermediates than CDOM*.

For PUHs degradation in an aqueous medium, the Fenton and Fenton-like processes are also commonly used and combined with advanced chemical, photochemical, and electrochemical oxidation processes [62–65]. The formation of reactive •OH radical is caused by the decomposition of H_2O_2 by Fe^{2+}, with the production of Fe^{3+}, which also catalyzes H_2O_2, what is known as Fenton-like reaction [66]. It can oxidize these herbicides by hydrogen abstraction from the molecules or by hydroxyl addition to them, forming highly reactive molecules (•R, •ROH) which can be further oxidized. These processes are dependent on the pH due to the different speciation of Fe ions, the optimum pH being around 3 [42].

Solid iron oxides can also be used as Fe sources in AOPs, with advantages due to their stability under irradiation, lower cost, and non-toxicity, the possibility of recovering, and no strict control of pH [63, 65]. The reduction of Fe^{3+} by H_2O_2 used to be slow, and in order to increase the oxidation efficiency and cost-effectiveness, Fenton's reaction can be electrochemically or photochemically catalyzed (electro-Fenton and photo-Fenton).

In Electro-Fenton reactions, Fe^{2+} is introduced in the medium as a catalyzer, then the electrochemical reduction of dissolved O_2 continuously generates H_2O_2 in situ. Two anodes, usually boron-doped diamond (BDD) and platinum (Pt), and carbon felt cathode have been used in studies for water treatment [44, 64, 67–70]. In photo-fenton oxidation processes, the photoreduction of Fe^{3+} to Fe^{2+} and the photochemical reactions of the complexes formed with Fe^{3+} ions increase •HO formation rate [71]. Phenylureas such as diuron, linuron, and isoproturón have been treated in water by this AOP [62, 63, 65, 72–75].

Although photocatalysis and Fenton processes are the most used AOPS for the degradation of PUHs in waters and soils, ozone is also an efficient oxidant as a source of hydroxyl radicals. These herbicides are decomposed by O_3 or can react with •OH radicals generated by O_3 decomposition. The effectiveness of ozonation is enhanced in combination with other oxidation conditions, such as some traditional oxidizing agents, UV irradiation or Fenton reagent [39, 41, 76–78].

Activated persulfate reactions have also been investigated due to their ability to degrade PUHs and other recalcitrant organic contaminants, such as pharmaceuticals, dyes, and halogenated compounds [79]. Persulfate needs to be activated by transition metals, heat or UV light to form the highly reactive sulfate radical. Vicente et al. [33] studied the diuron degradation and the removal of total organic carbon (TOC) (mineralization) from aqueous solution by persulfate activated with Fe^{2+} and observed the influence of temperature, persulfate, and Fe^{2+} concentration on the process. Xiong et al. [80] applied a weak magnetic field as an activator to Fe0 added persulfate to increase the removal of diuron in aqueous solutions.

Some of the studies of PUHs degradation in an aqueous medium carried out the comparison of several AOPs. Djebbar et al. [81] compared the following techniques for diuron degradation: Fe(III)/UV, Ferrioxalate/UV, Fe(III)/H2O2/UV, Ferrioxalate/UV/H2O2 and Fe(III)/H_2O_2 concluding that diuron oxidation was more increased with the systems Ferrioxalate/UV/H_2O_2 and Fe(III)/H_2O_2/UV than with Fe(III)/H_2O_2 and Fe(III)/UV. Fe(III)/UV was very efficient in diuron mineralization in solution compared to direct UV photolysis. Benitez et al. [82] used ozone, UV radiation, and some other AOP processes (O_3/H_2O_2, UV/H_2O_2, Fenton reagent, and the photo-Fenton system) to study the degradation of isoproturon, chlortoluron, diuron, and linuron determining kinetic parameters of each reaction between the phenylureas and the oxidizing systems. Kovács et al. [83] used ozonation, UV photolysis, heterogeneous photocatalysis and their combinations to study the oxidative degradation of diuron, fenuron, and monuron in water. They observed that for diuron and monuron, UV photolysis was highly efficient, while ozonation was more effective for fenuron transformation. The decomposition decreased as the number of chlorine atoms in the molecule increased in heterogeneous photocatalysis, and the addition of ozone to TiO_2-containing suspensions and UV-irradiated solutions increased the initial rates of degradation. The degradation of diuron and monuron was studied by Farkas et al. [84] using UV photolysis, ozonation, their combination (UV/O_3) and heterogeneous photocatalysis (TiO_2/UV). These authors concluded that UV/O_3 and TiO_2/UV were effective to reach the mineralization of both herbicides, in the order: $O_3 \ll TiO_2/UV < UV < UV/O_3$. They observed that the intermediates formed depended on the technique applied and that the presence of humic acid in the water acted, decreasing the degradation when using UV and UV/O_3, but enhanced the effect of only ozonation.

3.1.2 Abiotic Degradation in Soils

The natural attenuation of PUHs in soils is very slow, and there is a need of removing more quickly these herbicides and their by-products from soils, developing new strategies. Solarization has been proposed as a non-chemical remediation technique for the removal of pesticides in soils. Soil solarization is a natural hydrothermal disinfestation method for controlling soil-borne pathogens and weeds by passive solar heating. Chemical, physical, and biological changes are involved during solarization. It can accelerate the degradation and natural attenuation of pesticides residues in soil by photodegradation and, in some cases, by microbial proliferation as the temperature increases. However, in most cases, solarization was observed to change the soil microbial community structure and negatively impacted its activity and biomass [85]. This must be taken into account when solarization is used for pesticide degradation. Navarro et al. [86] reported the effect of solarization for dissipation of isoproturon using polyethylene film as a cover. Isoproturon disappeared at faster rates in solarized soils than in non-mulched soils, but they did not propose photodegradation as a degradation process for isoproturon because it is stable to photolysis. Fenoll et al. [87] used solarization and biosolarization (soil solarization + application of OM) for the dissipation of linuron from soils, observing similar results of both techniques on linuron dissipation curves. They attributed this behavior to the inactivation of microbial activity by solarization or to chemical degradation reactions occurring on humus and mineral particles of the soil.

In fact, the spontaneous abiotic degradation of PUHs in soils catalyzed by humic substances has also been observed for other pesticides in the environment [88]. The soil catalytic capacity on diuron hydrolysis in the soil/water mixture was evaluated by Salvestrini et al. [89–91], who suggested that the carboxylic and phenol groups of the soil OM can promote the hydrolysis of diuron. They concluded the phenylurea–humic acid interaction as a repartition-like equilibrium of phenylurea between humic acids and water, observing that the degradation rates of PUHs increased with HA concentration. Buffers such as acetate, carbonate or phosphate present or added to soil were highly efficient catalysts for this reaction.

Unlike the wide range of literature about the application of different techniques for the degradation of PUHs in water by oxidation processes, their application to the degradation in the soil is very scarce, and the few studies carried out using oxidation processes have been conducted at the lab scale [92]. Higarashi and Jardim [93] studied the remediation of soil contaminated by diuron using TiO_2 mediated by solar light under laboratory conditions. They observed that when soil contaminated with 100 mg kg^{-1} of diuron was irradiated for 50 h, the herbicide degradation was lower than 10%, but in the presence of TiO_2 as catalyzer (0.1%–2%) more than 90% diuron was degraded. The load of TiO_2 did not influence the degradation percentage and the degradation was limited to the first 4 cm of the soil.

A viable technology for the degradation of a variety of organic contaminants in soils is the chemical oxidation by Fenton's reagent. Pollutants such as PAHs [94], phenol [95] or DDT [96] have been removed from soil using the Fenton and Fenton-like processes. However, in relation to PUHs, only a few studies have been performed. Vicente et al. [97] used the Fenton-like reaction to degrade diuron, determining the influence of several concentrations of H_2O_2, the effect of Fe^{3+} as a catalytic species and the use of citrate as a chelating agent. When using H_2O_2 at 6 g kg^{-1}, the oxidation of diuron was about 55%. With the addition of 3 g kg^{-1} citrate as a chelating agent to mobilize iron from the soil to promote Fenton's reaction, up to 73% oxidation was reached. And finally, the addition of an extra amount of iron (0.6 g kg^{-1}) increased diuron oxidation up to 80%. Rosas et al. [98] continued the precedent study, establishing a kinetic model for diuron degradation which included the herbicide desorption rates, H_2O_2 decomposition by soil, citrate adsorption and diuron oxidation. Diuron oxidation was dependent on iron concentration and, to a lower extent, on H_2O_2 concentration.

In relation to chemical oxidation based on the effectiveness of persulfate (PS) free radicals (SO_4•−) for organic pollutants degradation, in the last years, this technique has extended its application for environmental remediation of pesticides, pharmaceuticals, halogenated compounds and dyes [79]. Persulfate has to be activated by heat, bases, transitional metals, UV, etc., but the activation with Fe(II) is the most common. However, as with the rest of abiotic degradation technologies previously mentioned, there are also very few studies concerning PUHs degradation. Vicente et al. [33] studied diuron oxidation and mineralization by persulfate activated with Fe^{2+}. They measured the degradation of diuron and the removal of TOC. The amount of Fe^{2+} added and the mode of addition (at the beginning of the reaction or as a continuous feeding) presented a high influence on diuron oxidation and mineralization. By continuously adding the iron solution at 50°C and using stoichiometric amounts of iron and persulfate, the complete degradation of diuron and 64% of TOC conversion were observed. Liu et al. [99] studied the isoproturon degradation in soil using chemical oxidation based on persulfate oxidants. Persulfate has to be activated, and they used Fe-based layered double hydroxide (LDH) as activators, instead of using Fe(II), which demonstrated a non-productive consumption of persulfate, or nanoscale zero-valent iron (nZVI), whose preparation was costly and with complex steps. They obtained the complete degradation of 500 mg kg^{-1} isoproturon in soil within 10 h. This technique was applicable in a broad pH range (3–11) and showed high tolerance to various inorganic anions (NO_3^-, HCO_3^-, Cl^-, Br^-) and humic acid. They observed that besides •OH and •SO_4^- radicals, singlet oxygen ($^1O_2$) and superoxide (•O_2^-) accounted for the oxidative degradation.

The application of O_3 to soils for pollutant degradation can be carried out "in situ" and "on site", and O_3 can be decomposed on soil active surfaces such as soil OM or metal oxides to generate •OH radicals. Some organic contaminants have been degraded with this technique, such as PAHs or petroleum contaminated soils [100, 101], but as far as we know, there are no studies about the application of O_3 to soils contaminated by PUHs.

On the basis of the above, it can be clearly deduced that the abiotic degradation of PUHs in the soil is possible, but it is still at a lab-scale stage and the different techniques used require many improvements before they can be applied even at a pilot plant level. Perhaps for this reason, and also due to the wide development of techniques based on biotic remediation of soils contaminated by PUHs, bioremediation technologies are much more extensively used.

3.2 Biological Remediation

Microbial activity is considered the main process related to the degradation of PUHs in soils [5, 102–104]. Pesticide microbial degraders are needed to achieve an ecological balance for soil contamination. The main factor which affects PUHs biodegradation is related to the magnitude of the bioaccessible fraction present in the soil, that is, the herbicide molecules in the soil solution or those weakly adsorbed on soil particles, which can become bioavailable for microbial degraders [105]. Bioavailability/biodegradation, as well as the general dispersion of pesticides in soils with mobility implications, including water and soil contamination, is mainly influenced by the sorption process. To date, as it can be observed in Table 2, there are several studies where biological technologies are used to eliminate PUHs.

Locke et al. [127] performed soil sorption and dissipation studies of fluometuron and its main metabolites in agricultural soils, concluding that higher capacity for fluometuron and metabolites sorption in no-tillage soils would be responsible for their longer persistence. Correlation between soil dissipation and soil OM content for two PUHs, chlortoluron and isoproturon, was found by Elgouzi et al. [106] who also concluded that the degradation rate was inversely correlated with soil pesticide sorption since strong sorption on soil particles would decrease the pesticide bioavailability. Zhu et al. [107] carried out studies on the formation of non-extractable residues in contaminated soils by the herbicide isoproturon, observing a lower formation of soil-bound residues when inoculated with a specific microbial degrader consortium.

3.2.1 Biostimulation

To increase the biodegradation of organic contaminants in the soil, the addition of nutrients (in particular phosphorus and nitrogen) and micronutrients (sulfur, iron, zinc, nickel, manganese, selenium, and cobalt, among others) is an important factor. The incorporation of organic residues into soils is a common practice to give nutrients and to improve soil physical, chemical, and biochemical properties. Many studies have shown that organic amendments affect the sorption behavior of pesticides present in the soil as well as their biodegradation [128–130]. Organic amendments' application on agricultural soils has not shown conclusive results about their influence on PUHs bioavailability and degradability. Romero et al. [131] evaluated the effects of soil treatments employing grape vermicompost and urea on diuron persistence in soil. They showed that the application of urea to the unamended soil decreased diuron persistence from 18.8 to 12.5 days, and from 33d

Table 2 Selected reports on the use of microbial remediation technologies for phenylurea herbicides in soil

Phenylurea	Soil	Contamination	Bioremediation Technique	Microorganisms	Achievements	Reference
Diuron	Agricultural soils	Artificially spiked soils	Biostimulant (Nutrient solution), Hydroxypropyl-β-cyclodextrin	Endogenous microbiota	Mineralization percentage increased in different soils in presence of HPBCD from 29.4, 1.8, 14.4, 16.5% to 41.9, 46.7, 27.1, 23.9%	[16]
Diuron	Agricultural soil	Artificially spiked soil	Biostimulation with urea and vermicompost	Endogenous microbiota	Urea decreased diuron persistence from 18.8 and 33 days to 12.5 and 15 days in unamended and vermicompost-amended soil, respectively	[95]
Isoproturon	Agricultural soil	Artificially spiked aged soil	Bioaugmentation	*Sphingomonas* sp. AK1 microbial consortium	*Sphingomonas* sp. AK1 or microbial consortium reached 28.7 and 46% of isoproturon mineralization after 46 days, respectively	[102]
Diuron	Six different soils	Artificially spiked soils	Biostimulation (micronutrients) and Bioaugmentation	*Arthrobacter sulfonivorans, Variovorax soli,* and *Advenella sp. JRO*	Mineralization of herbicide inoculating the consortium and nutrients solution was from 60.2 to 94.9%	[103]

(continued)

Table 2 (continued)

Phenylurea	Soil	Contamination	Bioremediation Technique	Microorganisms	Achievements	Reference
Diuron	Two agricultural soils	Aged contaminated soil (5 years' application) Artificially spiked soil	Natural attenuation	Endogenous microbiota	80.2% and 86.2% of biodegradation after 146 days (soils with over 5 years' application history) 34.4% and 48.4% of biodegradation after 146 days (soils without application history)	[104]
Chlortoluron and isoproturon	Agricultural (S5) and forest (S2) soils	Artificially spiked soil	Natural attenuation	Endogenous microbiota	65–85% in S5 and 47–62% of biodegradation in S2 after 100 days	[106]
Isoproturon	Agricultural soil	Artificially spiked soil	Bioaugmentation	Endogenous microbial community (MC) + *Sphingomonas* sp.	55.9% mineralized during 46 days	[107]
Diuron	Agricultural soil	Artificially spiked soil	Biostimulation (nutrients solution), amendments (sewage sludge (SS) and urban solid residues (USR)) and Hydroxypropyl-β-cyclodextrin	Endogenous microbiota	The best results were obtained when a mixture of nutrients, compost (SS or USR), and cyclodextrins were applied (from 15.5% mineralized to 46.5% and 33.2%, respectively)	[108]
Diuron	Agricultural soil	Artificially spiked soil	Bioaugmentation (microbial consortium) and	Endogenous microbial consortium (*Bacillus* sp., *Staphylococcus* sp.,	Diuron was completely removed when soil was	[109]

			biostimulation (vermicomposts)	*Brevundimonas* sp., *Achromobacter* sp., *S. epidermis., Ochrobactrum* sp., *Scopulariopsis* sp., *Acremonium* sp., *Fusarium* sp., and *F. solani).*	inoculated with the microbial consortium and vermicompost from olive-mill	
Isoproturon	Agricultural soil	Artificially spiked soil	Biostimulation (straw and compost)	Endogenous microbiota	The best result was reached when homogeneous compost was added: from 10% of mineralized to 20%	[110]
Chlortoluron	Agricultural soil	Artificially spiked soil	Biostimulation: amended with mushroom substrate (SMS) and green compost (GC)	Endogenous microbiota	14 mg of chlortoluron was completely eliminated after 273 and 67 days in unamended and amended soils	[111]
Diuron	Agricultural soil	Artificially spiked soil	Biostimulation (micronutrients), Bioaugmentation, Hydroxypropyl-β-cyclodextrin	Bacterial consortium of two exogenous strains *(Arthrobacter* sp. N2 and *Variovorax* sp. SRS16*)*	45% only with the consortium, 98% mineralized using bioaugmentation and HPBCD after 120 days	[112]
Diuron	Agricultural soil	Artificially spiked soil	Biostimulation (micronutrients) and Hydroxypropyl-β-cyclodextrin	Endogenous microbiota	66% mineralized after 100 days in presence of HPBCD 44% only with micronutrients	[113]

(continued)

Table 2 (continued)

Phenylurea	Soil	Contamination	Bioremediation Technique	Microorganisms	Achievements	Reference
Diuron	Ten sterilized agricultural soils	Artificially spiked soils	Biostimulation (micronutrients) and Bioaugmentation	Exogenous bacterial consortium	Microbial consortium showed to be effective to increase the mineralization diuron in different agricultural soils	[114]
Isoproturon	Agricultural soil	Artificially spiked soil	Bioaugmentation and co-metabolism (Casamino acids)	*Sphingomonas* sp. SRS2	100% biodegraded and 50% mineralized after 15 days	[115]
Diuron	Agricultural soil	Artificially spiked soil	Bioaugmentation	*A. globiformis* D47 and *Variovorax* sp. SRS16 individually or in a coculture	5.9% mineralized inoculating the strain D47, 36.6% with SRS16 individually, and 59.9% when both strains are inoculated	[116]
Isoproturon	Agricultural soil	Artificially spiked soil	Bioaugmentation	*Sphingomonas* sp. SRS2	90% biodegraded in sterilized soil in presence of *Sphingomonas* sp. SRS2	[117]
Isoproturon	Rhizospheric soil	Artificially spiked soil	Bioaugmentation	*Pseudomonas aeruginosa* JS-11.	The herbicide was completely degraded within 20 days	[118]
Isoproturon	Nine agricultural soils	Artificially spiked soils	Natural attenuation	Endogenous microbiota	30–40% of isoproturon was mineralized	[119]

Isoproturon	Three agricultural soils	Artificially spiked soils	Natural attenuation	Endogenous microbiota	In wheat-cotton 13.73 to 73.76% of dissipation, In wheat-maize crop rotation, dissipation was from 23.96 to 79.88%- and the agricultural field was from 13.48 to 71.11% after 2 weeks	[120]
Diuron	Sterilized saline soil	Artificially spiked soil	Bioaugmentation	*Stenotrophomonas rhizophila* CASB3	94% biodegraded in 42 days	[121]
Diuron	Farm soil (uncontaminated)	Artificially spiked soil	Bioaugmentation	*Neurospora intermedia* DP8–1 (fungi)	18.2% biodegraded in fresh soil, 30.3% in fresh soil + DP8–1 16.3% biodegraded in sterile soil and 41.9% in sterile soil + DP8–1 after 20 days	[122]
Diuron	Agricultural soil	Artificially spiked soil	Bioaugmentation	*Bacterial strain identified as D47*	At a density of 9.3×10^6 CFU g^{-1}, 15 mg kg^{-1} biodegraded after 16 days	[123]
Diuron	Agricultural soil	Artificially spiked soil	Biostimulation (micronutrients) and Bioaugmentation	Exogenous bacterial consortia from five agricultural soils/ Hydroxypropyl-β-cyclodextrin	13% mineralized with only micronutrients, 27% with HPBCD, 23% with the most effective consortium, 42% with HPBCD + the selected consortium	[124]

(continued)

Table 2 (continued)

Phenylurea	Soil	Contamination	Bioremediation Technique	Microorganisms	Achievements	Reference
Diuron	Agricultural soils	Aged contaminated soil (3 years' application) and uncontaminated soil	Natural attenuation	Endogenous microbiota	68.95 μg · 100 g^{-1} of soil were mineralized after 64 days (soil treated for 3 years) 24.16 μg · 100 g^{-1} of soil were mineralized after 64 days (uncontaminated)	[125]
Diuron	Experimental farm soil	Artificially spiked soil	Bioaugmentation	*A. globiformis* D47	45.8% biodegraded after 30 days	[126]

to 15 days in the vermicompost-amended soil, which was attributed to the improvement in dehydrogenase enzyme activity after vermicompost application. Fernández-Bayo et al. [132] also observed that the addition of vermicomposts from wastes of wine and alcohol industries to soils decreased the persistence of diuron, and the presence of the metabolites DPMU and DPU was detected. Rubio-Bellido et al. [108] found out that the phenylurea diuron was mineralized at a higher rate when the compost was applied on the contaminated soil, concluding that this was due to the addition of specific diuron degraders, initially present in the organic amendments, the presence of bioaccessible organic nutrients from the compost, the presence of (DOM) which would act as a natural extractant that increases the concentration of diuron in the soil solution, and the compost which could be used as a carbon source by soil microbiota. Castillo-Díaz et al. [109] observed that vermicompost application gave rise to an increase in the number of microbial diuron degraders, accelerating the capability of soil diuron dissipation. Vieublé Gonod et al. [110] performed experiments to determine the impact of straw and compost application on isoproturon mineralization and the obtained results showed that the addition of exogenous OM stimulated microbial activity, which increased herbicide mineralization. Marín-Benito et al. [133] observed that DT50 values for linuron decreased (1.6–4.8 times) in a soil amended with grape marc, spent mushroom substrate or sewage sludge, relative to the unamended soil, and they demonstrated the no correlation between DT50 values and sorption coefficients and that chemical hydrolysis could explain the rapid dissipation of linuron.

By contrast, the application of organic amendments can also decrease the bioavailability of pesticides due to pollutants sequestration within the soil organic matrix. Grenni et al. [134] observed a lower linuron degradation rate in oak- and pine-amended soils in comparison with unamended ones, and also Marín-Benito et al. [111] observed that the use of organic amendments decreased the degradation rate of the herbicide chlortoluron due to its higher sorption, and hence, lower bioavailability for degradation in amended soils. The conclusion that can be extracted from all these studies is that the use of amendments in PUHs contaminated soils requires previous studies to observe the persistence of each herbicide in relation to each amendment used.

Another strategy to increase the bioavailability of organic pollutants in soils, and therefore their biodegradation, is the addition of extractant solutions, and in the case of PUHs, cyclodextrins (CDs) have been used as bioavailability enhancers [135]. In addition, CDs biostimulate the soil microbial activity because they are highly biodegradable, also acting as carbon sources [136]. Cyclodextrins (CDs) are compounds formed by cyclic oligosaccharides obtained by enzymatic degradation of starch. They have the capacity of forming inclusion complexes thanks to their chemical structure showing a hydrophobic cavity that can encapsulate hydrophobic compounds through host–guest interactions, such as Van der Waals forces or hydrogen bonds [137]. This interaction can occur between the cavity of the CD and the hydrophobic part or the whole molecule of the guest. CDs have been used as solubilizing agents for a wide variety of pesticides [138–143] facilitating their subsequent desorption and degradation in soil [144–148]. Smith et al. [149]

described the complexation between four PUHs, metobromuron, monolinuron, monuron and fenuron, and α- and β-CDs in solution by NMR spectroscopy, concluding from the observed chemical shifts that in all cases only the guest aromatic ring enters the host cavities. Sakina et al. [150] studied the inclusion complex formed between β-CD and the herbicide metobromuron, concluding that the aromatic ring is deeply included inside the β-CD cavity, and also intermolecular hydrogen bonds are established between guest and host molecules. The inclusion complexes formation results in an increase in the hydrosolubility of the organic compound, provoking that a higher amount of molecules are present in the soil solution, in other words, its bioavailable fraction in the contaminated soil is increased. For this reason, CDs have been used for bioremediation purposes in contaminated soils by different organic pollutants, and in particular, as bioavailability enhancers of PUHs. Villaverde et al. [112] were able to improve the soil diuron mineralization rate. Diuron is a PUH that shows a high persistence in soil due to its reduced bioavailability. In that work, HPBCD was those CD that showed the best complexation results with diuron and it was used for remediation of the herbicide contaminated soil, where the joint application with an artificial microbial consortium degrader provoked the complete removal of diuron. Villaverde et al. [113] proved that the use of a concentration of HPBCD solution that is equal to 10 times the concentration of diuron contaminating the soil is capable of acting as a bioavailability enhancer that accelerates the passage of the herbicide fraction weakly adsorbed on soil particles to the soil solution, improving the accessibility of the herbicide by the microorganisms. Rubio-Bellido et al. (16) studied the effect of HPBCD on diuron desorption, leaching, and mineralization in soils and determined that an increase in diuron mineralization was due to its higher bioavailability. Rubio-Bellido et al. [114] showed the existence of a significant correlation between a bioaccessible soil fraction, determined by non-exhaustive extraction techniques, and the capacity of a specific diuron microbial degrader to mineralize the herbicide.

3.2.2 Bioaugmentation

With the aim of improving the degradation of PUHs, studies have been focused on the isolation and identification of different degrading microbial populations from adapted soils. Sometimes soil microbial population is not adequate or its concentration is too low to efficiently biodegrade the herbicide. In such situations, the inoculation of the soil with specific degrader strains of these herbicides to increase their degradation rates is carried out. This is called bioaugmentation. Consortia of mixed bacterial cultures or pure bacterial strains have been isolated for phenylurea degradation [115–119, 151–155]. Studies have been published on isolating individual microbial strains capable of degrading different PUHs. Ngigi et al. [156] isolated different bacterial strains of the genera *Burkholderia*, *Bacillus,* and *Vagococcus* from agricultural soil that had been managed with PUHs under repeated applications. The isolated *Vagococcus fluvialis*, *Bacillus* spp., *Bacillus cereus,* and *B. ambifaria* were capable of degrading diuron in the range from 19% to 25% of the herbicide in solution (40 mg L^{-1}) after 35 days of incubation, but small amounts of 3,4-DCA and DCPMU metabolites were also detected after the inoculation assay. Abbas et al. [120] isolated an isoproturon degrading bacterial strain designated as *Sphingobium* spp. S29 from an agricultural site. This strain was capable of not only degrading isoproturon but also its known metabolites and other PUHs including chlortoluron and diuron. Muendo et al. [104] isolated bacterial strains capable of degrading diuron, *Bacillus*, *Pseudomycoides*, and *B. muralis*/*B. simplex*, using the enrichment culture degraders isolation technique with pineapple and sugarcane-cultivated soils with a history application of the herbicide during 5 years and using diuron as the only carbon source, but the metabolites 3,4-DCA and DCPMU were detected after 46 days of incubation.

Sorensen et al. [115] isolated a strain identified as *Sphingomonas* sp. from an isoproturon-treated agricultural soil which is capable of mineralizing isoproturon, although other metabolites were also determined. Also, this strain was observed to degrade diuron and chlortoluron herbicides obtaining unidentified products. Sorensen et al. [157] were able to isolate *Variovorax* sp. from agricultural soils employing an enriched liquid culture of linuron as the sole carbon and nitrogen source, and they observed that *Variovorax* sp. mineralized the herbicide. Most works show the need of using a microbial consortium for effective biodegradation of PUHs. Li et al. [102] studied isoproturon degradation in an agricultural soil through the inoculation with an individual isolated bacterial strain degrader, *Sphingomonas* sp. strain AK1, or a microbial consortium where this individual strain was included, and they concluded that microbial consortia were more efficient to improve the removal of organic pollutants in soil than individual degrader strains and that it might maintain the degradation ability in soil over a longer period, since the soil microbial community helps to keep the nutritional requirements in soil. A similar conclusion was also reached by Zhang et al. [158]. In this study, the bacterial strain *Diaphorobacter* sp. LR2014-1, capable of initially hydrolyzing linuron to 3,4-dichloroanaline and *Achromobacter* sp. ANB-1, which has the ability to mineralize the different anilines formed, was applied individually and as a consortium. Synergistic biodegradation of linuron by the consortium resulted in more efficient degradation of the herbicide than when these strains were applied individually. Silambarasan et al. [121] employed a diuron-degrading *Stenotrophomonas rhizophila* strain CASB3 tolerant to salinity, isolated from *Fragaria ananassa* roots. Complete degradation of diuron in aqueous medium under normal conditions was observed within 48–120 h, and under salinity stress conditions within 48–192 h. When bacterial degrader strain CASB3 was applied to a diuron-contaminated saline soil, 94% diuron was efficiently degraded in 42 days. Wang et al. [122] isolated the diuron-degrading endophyte DP8-1, identified as *Neurospora intermedia* from sugarcane root grown in diuron treated soil, achieving up to 99% diuron biodegraded within 3 days. The work also showed that the strain DP8–1 was capable of using metobromuron, isoproturon, fenuron, monuron, linuron, chlorbromuron, and chlortoluron as a substrate for its growth. The inoculation of strain DP8–1 into a diuron-contaminated soil enhanced the rate of diuron dissipation (Table 2). Cullington and Walker [123] employed the liquid enrichment culture technique to obtain a bacterial isolate from soil able to degrade diuron. The addition of this isolate at 9.3×10^6 cfu g^{-1} to soil reached a DT50 value of 2–6 days for diuron, but it was also able to degrade other phenylureas in liquid culture in the order linuron > diuron > monolinuron >> metoxuron > isoproturon.

Villaverde et al. [103] studied the ability of an artificial herbicide degrading microbial consortium for achieving the mineralization of diuron in solution and in soils with different properties. Almost a complete removal of diuron in solution was achieved when inoculated with the consortium (98.8%) after only a few days. The bacterial consortium used was composed of the following diuron-degrading strains: *Arthrobacter* sp. N2, *Variovorax* sp. SRS16 and *Advenella* sp. JRO, showing the capacity of a member of the genus *Advenella* to remove diuron for the first time from contaminated soils. None of the three studied bacterial strains individually applied was capable of mineralizing the herbicide diuron in solution.

Villaverde et al. [124] also studied diuron mineralization activity of five diuron-degrading microbial consortia (C1-C5), each of them isolated from agricultural soils. The best results were observed when C2 was employed, reaching 81.6% diuron mineralization in solution. These consortia were also used in soil suspension systems, and DT50 was significantly reduced from 700 days (non-inoculated control) to 171 days for the most effective microbial consortia in soil, C1. Also, the isolated consortium C1 was inoculated for soil diuron mineralization in more realistic soil conditions (40% of soil water-holding capacity), and an important improvement of diuron mineralization was observed reaching 23.2% as against 13.1% in the non-inoculated assay.

Although most microbial degradation studies of PUHs are focused on bacteria, fungi have also been shown to degrade them. Ellegaard et al. [159] observed in the diuron biodegradation studies with five *Mortierella* strains that their ability of degradation varied greatly among the strains proved. The authors concluded that diuron degradation by *Mortierella* was a co-metabolic process, but the accumulation of its metabolites was observed, suggesting that the incorporation of both fungal and bacterial strains would be a possible solution for achieving complete biodegradation of diuron.

Within the published works related to phenylurea biodegradation in soil, Bending and Rodríguez-Cruz [160] studied the effect of soil depth in the biodegradation of the herbicide isoproturon, concluding that the observed decreasing biodegradation rates with soil depth were not due to the starting population size of degrader organisms, but to an increase of the lag phase, suggesting that degradation rates were controlled by the time required for adaptation of the endogenous microbiota.

3.2.3 Phytoremediation

The use of plants for removing pollutants from contaminated soils and water (phytoremediation) has gained importance from an economic and environmental point of view due to its effectiveness as in situ technology. PUHs, as previously commented, can be considered persistent in soils with high OM contents. Although

PUHs can be partially biodegradable in soil, a portion can remain as their metabolites in the form of chloroanilines, which have higher toxicity and recalcitrance. For phytoremediation, cereal crops would be a good option because they are resistant due to their metabolic characteristics. For example, to get a suitable uptake of the phenylurea isoproturon by the plant root in phytoremediation experiments, the use of biosurfactants such as rapeseed oils or esters should be included. Likewise, it has been suggested to leave the contaminated area as fallow, with the aim of decreasing the soil OM content with time making PUH residues more bioaccessible to soil organisms or plant roots [161].

Another limiting factor for phytoremediation application is the potential toxicity of the pollutants to the plants used [162]. To overcome this, the use of genetically modified plants more resistant to the toxicity of PUHs and their potentially formed metabolites in soil and plant is gaining importance in phytoremediation. In this sense, Didierjean et al. [163] worked on the Jerusalem artichoke (*H. tuberosus*) xenobiotic inducible cytochrome P450, CYP76B1, and observed that it catalyzed the oxidative dealkylation of several PUHs to non-phytotoxic metabolites, and hence, increasing tolerance, which may be achieved by ectopic constitutive expression of CYP76B1 in tobacco (*Nicotiana tabacum*) and *Arabidopsis*. Modification with CYP76B1 on tobacco and *Arabidopsis* increased the tolerance to linuron by 20-fold and to chlortoluron and isoproturon by ten-fold. Dosnon-Olette et al. [164] investigated the ability of ***L. minor*** to eliminate the herbicide isoproturon. The toxicity of isoproturon is concentration-dependent regardless of the chlorophyll fluorescence and growth rate. The authors observed a removal capacity of 25% of isoproturon after 4 days of the assay because of the presence of ***L. minor***. Okhawa and Inui [165] employed transgenic plants capable of expressing cytochrome P450 enzymes with the aim of achieving herbicide tolerance as well as phytoremediation of different phenylurea and sulfonylurea herbicides. Jang et al. [166] investigated the use of transgenic ginseng derived PgCYP76B93 in *Arabidopsis* for phytoremediation of PUHs. The bioassay with transgenic plants showed an enhancement in the resistance against chlortoluron. However, the main problem of using transgenic plants is that they can also accumulate and release intermediate metabolites causing phytotoxicity or additional environmental problems.

Another way to diminish pollutant toxicity on plants used for phytoremediation is the use of plant growth regulators [167]. Lu et al. [168] described the enhancement of isoproturon degradation in the wheat rhizosphere when treated with salicylic acid. Soil amendments can be also used as growth-inducing agents. For example, Ferreira et al. [169] tested phytoremediation using species of green manure amended with vinasse for tebuthiuron removal from soil, showing that *M. pruriens* and *P. glaucum* have the capacity of effective phytoremediation in soils contaminated by this herbicide.

Yan et al. [170] performed a research to give value to the synergistic relationship between a genetically modified *Arabidopsis* plant for expressing the bacterial N-demethylase PdmAB and the inoculated biodegrading bacterium, *Sphingobium* sp. strain 1017-1 in the rhizosphere. The combination of transgenic plant and microbe remediation system showed to be efficient, and a complete dissipation of PUHs from contaminated sites could be achieved.

4 Summary and Conclusions

Due to the serious environmental and public health problems provoked by the use of PUHs in agricultural practices, a great variety of biotic and abiotic techniques have been developed to degrade and remove them from soils. The present review gives an overview on the technologies used to degrade PUHs in contaminated soils. The fundamentals of each technology are analyzed and their advantages and disadvantages, application limits and advances, as well as their future research prospects are discussed.

The majority of the degradation techniques developed are biotic, and bioremediation techniques have shown to be successful to deal with this concern. Significant advances in the use of bacteria for PUHs cleaning up processes have occurred in the last 20 years. Strategies such as bioaugmentation, using the soil microbial community adapted to PUHs in contaminated soils, biostimulation (including organic amendments) and the use of defined mixed cultures were developed to enhance their bioremediation. A great variety in the genera of PUHs-degrader bacterial strains has been published, but Bacillus sp. is the most common, highlighting their important role in PUHs degradation in soil. On the contrary, the use of fungal strains to degrade PUHs has been much less studied, and this is probably a research gap in their remediation in soils, as well as the use of both fungal and bacterial strains simultaneously. The main factor which affects PUHs biodegradation is related to the magnitude of the bioaccessible fraction present in soil, mainly influenced by the sorption process, with a clear correlation between soil dissipation and soil OM content. In this sense, the addition of extractant solution to the contaminated soils, with special mention of CDs in the case of PUHs, has been used as bioavailability enhancer. In spite of the progress made in bioremediation, most of the research concerning this issue is limited to laboratory scale studies, and there is a lack of field experiments. Phytoremediation techniques based on the interactions between microorganisms and plants are another promising alternative proposed as an ecofriendly method for cleaning up PUHs-polluted soils.

For the future, in relation to biotic degradation of PUHs, further studies should be conducted to apply advanced omics based approaches to identify the genes and enzymes involved to discover the enzymatic and genetic basis of their microbial degradation. Such genetic information will further serve as baseline for genetic engineering of the PUHs-degrading microbial strains to enhance their potential.

PUHs abiotic degradation has been considerably studied under in vitro conditions in liquid cultures, but there are not many studies of such degradation in soil. These studies have been carried out using oxidation processes but only at lab scale.

In general, the remediation technologies exposed have been proved to be successful at laboratory scale, but a more in-depth evaluation in large-scale experiments under in situ field conditions is needed. This would provide information on the success of the different developed technologies and their impact on the soil ecosystem, and would allow calculating the cost–benefit relation of each technology to be fully addressed.

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Bioremediation of Soil Ecosystems from Triazine Herbicides

Anna Barra Caracciolo and Paola Grenni

Contents

Abstract Microorganisms play an important role in maintaining ecosystem environmental quality, including pesticide removal from soil and water. Triazine herbicides are among the most commonly used pesticide worldwide. Moreover, they are ubiquitous soil and water contaminants. Atrazine, simazine, and terbuthylazine removal from environment depends on abiotic (photolysis and hydrolysis) and above all biotic degradation; only the latter is able to mineralize these herbicides. The presence of an abundant and varied microbial community is a necessary prerequisite for a prompt and effective triazine elimination from contaminated soil and water. Degradation rates can be highly variable, depending on the history of the herbicide treatment and on site-specific characteristics (e.g., soil depth, texture, mineralogy, organic carbon (OC) content, and pH). Several microorganisms able to remove atrazine from soil and water have been identified and can be used for bioremediation (bioaugmentation and biostimulation) purposes. They comprise prokaryotic cells and fungi which can use triazines for growth (catabolic degradation) or transform these herbicides by cometabolism. Some plants can partially degrade and detoxify triazines, however the effectiveness of phytoremediation in removal of

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triazines is hampered by their intrinsic toxic effects (they act on photosynthesis and glycogenesis, inhibiting the photosystem II) and depends on a plant capability to resist to its biocide effect and to form synergic interactions with microorganisms.

Keywords Atrazine, Bioaugmentation, Biodegradation, Biostimulation, Chloro-*s*-triazines, Nature-based solutions, Simazine, Terbuthylazine

1 Introduction

Pesticides are chemicals used in agriculture and in other non-agricultural areas, for controlling pests and diseases which would otherwise reduce agricultural yields or hinder other processes. Pesticides include bactericides, fungicides, algicides, herbicides, nematicides, molluscicides, acaricides, insecticides, and rodenticides. In particular, herbicides are a class of pesticides used for killing or controlling plant growth, used for weed or grass killer [1].

Only in Europe, the amount of pesticide sold is about 360 million kilograms per year [1]. The main agricultural EU producers are France, Spain, Italy, and Germany. Most herbicides are xenobiotics, i.e. foreign chemicals to humans and ecosystems and they can be classified in accordance with the active substance, which causes the desired biological effect.

In particular, triazines are a large family of worldwide used class of herbicides for controlling broadleaf weeds and annual grasses in various crops (e.g., corn, sorghum, sugarcane), residential lawns, and golf courses [2]. Triazines consist of a nitrogen-containing heterocycle, with the same core structure, i.e. an aromatic ring of three carbon atoms and three nitrogen atoms arranged alternately to provide three-fold rotational symmetry.

Chloro-*s*-triazines (symmetrical 1,3,5-triazines with a chlorine atom at the 2-position of the ring) perform their biocide action inside a plant, after root absorbing, inhibiting various biochemical processes, above all photosynthesis in leaves [3] and glycogenesis, and specifically inhibiting the photosystem II. Their selectivity is based on the inability of plants of metabolizing or detoxifying herbicides. They can be used both in pre-emergence and post-emergence weed control, alone or mixed with other herbicides. Main triazine herbicides are atrazine, simazine, and terbuthylazine and they differ only in the *N*-alkyl side chains (R_1 and R_2), (Fig. 1).

Triazines compounds with low water solubility and low volatility compounds; they can be adsorbed to soil by cationic exchange because of its susceptibility to protonation; this process is favored by pH decrease [4]**.** Owing to their use in high amounts (e.g., terbuthylazine is applied at about 750 g active ingredient ha^{-1}) [5, 6] and the fact that only a fraction ($<1\%$) of the applied dose reach the target sites within plants, they are diffuse soil contaminants [7]. Moreover, persistent parent compounds and/or their metabolites can reach from soil surface water or groundwater through runoff and leaching phenomena, respectively [8, 9].

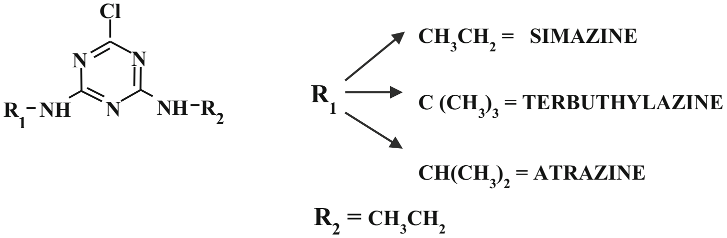

Fig. 1 Chemical structure of simazine, terbuthylazine, and atrazine

European Union banned atrazine and simazine since 2003 and 2004, respectively. However, these herbicides together terbuthylazine and their deethylated metabolites are found in water bodies, with concentrations higher than 0.1 μg L^{-1} (maximum admissible concentration under the drinking-water legislation: Council Directive 98/83/EC) [10].

Atrazine and simazine are still used in USA, Brazil, Australia, China, and India. In the USA, atrazine is classified as a restricted-use herbicide; a national survey on groundwater over a 20-year period (1993-2011) revealed simazine and atrazine among the most detected pesticides [11] in agricultural and urban wells owing to its extensive applications in all land-use settings. In many cases, desethyl-atrazine, a degradation product of atrazine, was detected more frequently than its parent compound [12]. Concentrations of atrazine in drinking water of the USA were found up to 3.0 μg L^{-1} [13].

Atrazine (6-Chloro-4-*N*-ethyl-2-*N*-propan-2-yl-1,3,5-triazine-2,4-diamine) has been sold in the market since 1950s. It can be used alone or in mixture with other herbicides for agricultural applications for pre- and post-emergent control of broadleaf and grassy weeds [14–16]. It has been banned in Europe for its intrinsic toxicity and occurrence in ground and surface water at concentrations above legal limits [17–21]. Atrazine is still one of the most used worldwide pesticides with annual consumption of about 70,000–90,000 tons [22, 23]. Only in the USA about 33,000 tons of atrazine is applied annually in agriculture [24].

Atrazine has been reported to exhibit reproductive toxicity in mammals and other animals [25–28], to be an endocrine disruptor and linked to Parkinson disease in humans [29, 30].

Atrazine and its main metabolites (desethyl-atrazine and deisopropylatrazine) are commonly detected as water contaminants, and their residual concentrations can be found both in soil and water for a long time after its application for agricultural or industrial purposes [31, 32]. Atrazine removal from the environment depends on abiotic (photolysis and hydrolysis) and above all biotic degradation, although only the latter is able to mineralize this herbicide. Several microorganisms able to remove atrazine from soil and water have been identified [7, 32, 33].

Simazine (6-Chloro-2-*N*,4-*N*-diethyl-1,3,5-triazine-2,4-diamine) has been used since 1955 on a variety of crops. In the USA it is used for turfgrass, ornamentals (trees), field crops, and fruit crops [12]. In a similar way of atrazine, simazine and its deethylated metabolite, desethyl-simazine (DES) are commonly found as water and groundwater contaminants [34]. Simazine toxicity has been recognized and for this reason has been included in the EU Priority Pollutant List [35]. Simazine has also been classified as genotoxic and as a possible carcinogenic compound by EPA [36]. The metabolite DES conserves phytotoxic properties of its parent compound [37].

Terbuthylazine (2-*N*-tert-butyl-6-chloro-4-*N*-ethyl-1,3,5-triazine-2,4-diamine) is the only triazine herbicide currently in use in Europe in accordance with EC Regulation 1107/2009 (repealing 91/414). However, European Food Safety Authority (EFSA) has reported that terbuthylazine poses high long-term risks for mammals, aquatic organisms, non-target plants, and earthworms [38] and can have genotoxic effects [39]. In a similar way with atrazine and simazine, one of the primary mechanisms of its transformation is a biotic oxidative *N*-deethylation with the formation of desethyl-terbuthylazine (DET) [40]. Terbuthylazine and its toxicological relevant metabolite DET pose a risk both for the environment and human health. Monitoring data show that DET is frequently present in groundwater and its concentration is often higher than its parent compound. This phenomenon is due to the intrinsic characteristics of DET (e.g., water solubility and soil OC partition coefficient) which determine its lower adsorption and higher mobility in soils [41–45].

Terbuthylazine (TBA) is generally found to halve in a surface active soil at 20°C in about 30 days, at initial concentration of 1–5 mg kg^{-1}. However, its persistence in soil can be quite variable (half-life time (DT_{50}) ranging from 20 to 180 days) depending on site-specific characteristics [46]. The more TBA is degraded in soil, the less the likelihood of it being leached to groundwater or run off to surface water. Degradation rates in agricultural soils depend on the history of terbuthylazine treatment, which can increase soil self-remediation potential in terms of selection of microbial populations able to metabolize it [47, 48]. However, specific soil characteristics (e.g., soil depth, texture, mineralogy, OC content, and pH) affect significantly the biodegradation process. Herbicide degradation is favored in the surface soil where a higher microbial abundance and activity is present [40, 49, 50]. For example, TBA halved at 22°C with very different degradation rates, considering two soil depths of the same agricultural soil (DT_{50} at 5–25 cm = 30 days; and DT_{50} at a 40–60 cm = 180 days). The significant slower degradation in subsoil was ascribable to a lower microbial abundance. In the same soil, a decrease in temperature (from 22 to 15°C) slowed down the degradation activity of surface soil microroganisms and the same amount of TBA was degraded with similar values (c.a. 200 days) between soil and subsoil [40, 51]. These results suggest that in some parts of the world where the soil average temperature is low, a higher triazine persistence is expected. Water content and presence of exogenous nitrogen [43, 52] and organic amendments [50] can also directly or indirectly influence the degradation process. Finally, soil texture and mineralogy can affect TBA degradation, influencing microbial activity. In particular, microcosm experiments showed how high DT_{50} values (95–105 days) were found in a clay-loam soil owing to the presence in its clay of mineral montmorillonite. The latter has a great capacity to adsorb organic matter (OM) [53], including triazine herbicides, decreasing their bioavailability for degradation [50, 54].

2 Biodegradation as a Regulating Ecosystem Service Provided by Microorganisms

Microbial communities play key roles in natural ecosystem functioning, such as primary production, OM decomposition, nutrient cycling, and removal of contaminants, and thus contribute to soil and water purification processes, providing key regulating ecosystem services. The maintenance of these ecosystem services is linked to that of bacterial diversity and functioning [55]. Microorganisms can degrade and use triazine as a source of both carbon and nitrogen for growth (catabolic degradation). In other cases microorganisms degrade pesticides by a co-metabolic action [56].

However, degradation rates can be highly variable, depending on the history of an herbicide treatment and on site-specific characteristics. Although triazines can be degraded through both abiotic and biotic processes, only the latter make it possible their complete removal from ecosystems.

The degradation of atrazine, simazine, and terbuthylazine follows similar pathways. A common step is the formation of hydroxyl metabolites (2-hydroxyatrazine, 2-hydroxysimazine, and 2-hydroxyterbuthylazine), which can occur through abiotic chloro hydrolysis, under acidic or alkaline conditions, or thanks to microbial enzymes. Only microbial degradation leads to dealkylated metabolites (desethyl-atrazine, desethyl-simazine, and desethyl-terbuthylazine). Subsequently, non-biological and biologically mediated dehalogenation processes can convert dealkylated metabolites to their corresponding hydroxylated forms.

Main knowledge on the degradation mechanisms of triazines derives from studies involving atrazine. Complete atrazine biodegradation (mineralization) can occur through six enzymes encoded by highly conservative genes, such as *atz*A, *atz*B, *atz*C, *atz*D, *atz*E, and *atz*F. These genes have been found firstly on a plasmid of *Pseudomonas* sp. ADP [57], which is considered the reference strain. Subsequently, these genes have been detected in other several transmissible bacterial plasmids; however, not all six genes are always present in the same bacterium. For example, Barra Caracciolo et al. [49] isolated from a contaminated groundwater two bacterial strains *Advenella incenata* and *Janthinobacterium lividum,* which had the *atz*A, *atz*B and *atz*B and *atz*C genes, respectively (Fig. 2). In another work Grenni et al. [58] isolated from the same groundwater the bacterium *Rhodococcus wratislaviensis* (Fig. 3), which had the overall six degrading genes; in fact, it was able to mineralize terbuthylazine, simazine, atrazine, 2-hydroxysimazine, desethyl-atrazine, isopropylamine, and ethylamine [49, 58].

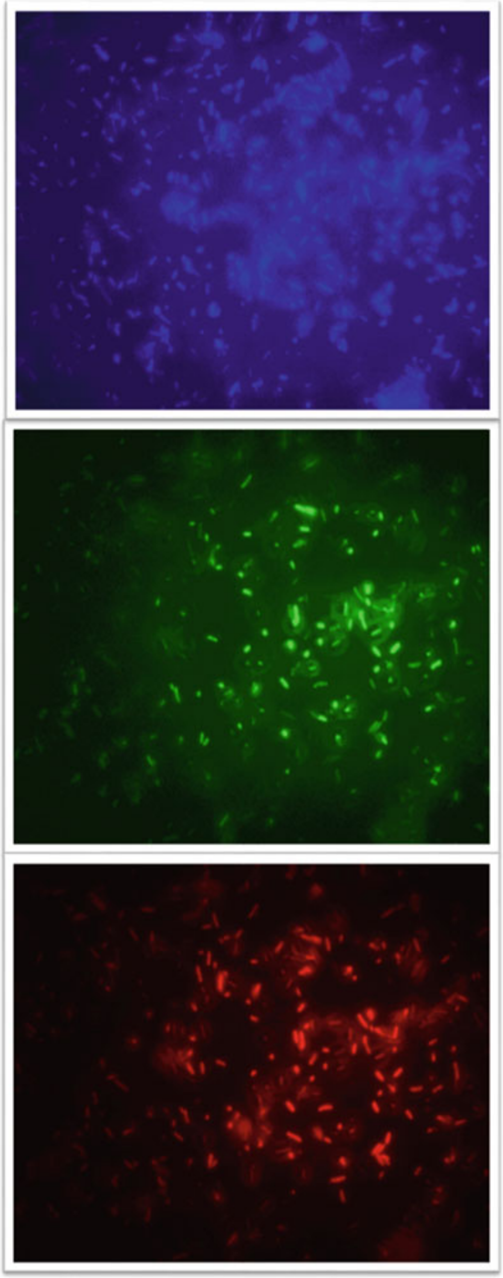

Fig. 2 Photo of a pure culture of *Janthinobacterium lividum* (Beta-*Proteobacteria*) able to degrade terbuthylazine, examined with the Fluorescence In Situ Hybridization technique with different oligonucleotide probes. Total bacterial cells (DAPI stain in blue color); cells stained with *Proteobacteria* (EUBI-III) probes, labeled with FAM (green color); cells stained with Beta-*Proteobacteria* probe labeled with Cy3 (red) [49]

Currently, numerous bacteria have been isolated using triazines as a nitrogen or carbon source. In some cases, the hydrolytic pathway (*atz*A) catalyzed by a chlorohydrolase can be performed by an alternative enzyme (hydrolase) encoded

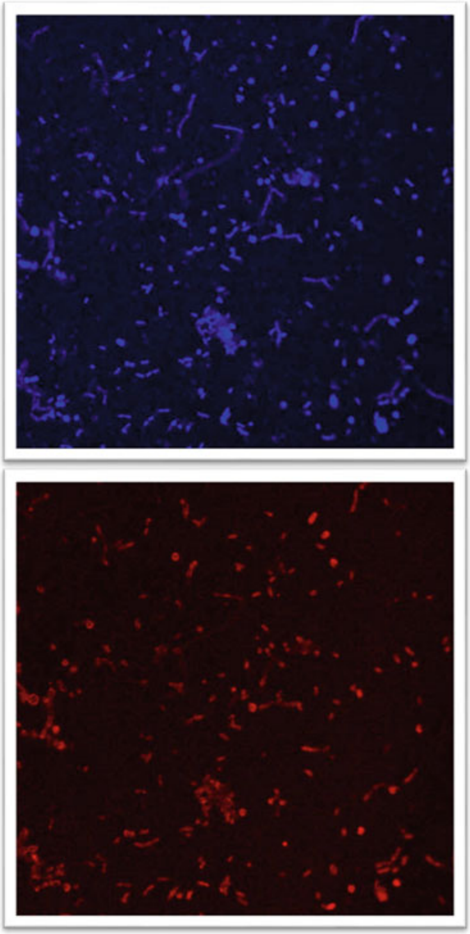

Fig. 3 Photo of a pure culture of *Rhodococcus wratislaviensis* strain FPA1 (*Actinobacteria*) able to mineralize terbuthylazine and triazines, examined with the Fluorescence In Situ Hybridization technique with DAPI stain (blue color) and the specific oligonucleotide probe RhLu labeled with Cy3 (red) [58]

by the *trz*N gene. The formation of cyanuric acid as an intermediate and then its transformation to biuret is generally the step before mineralization. However, the sequence of pathway steps varies among degraders and can depend on the environmental availability of carbon and nitrogen sources [43, 49, 52, 59, 60]. The bioremoval of the tertbuthyl group is not common in terbuthylazine, because it can be inhibited by its steric hindrance or this process cannot take place due to the absence of any hydrogen atom bonded to the tertiary carbon one. The tertbuthyl removal can occur just before ring cleavage [40].

Biodegradation and mineralization of triazines can be carried out by both bacterial consortia and single strains [49, 50, 58]. Several bacteria able to degrade triazines were isolated from both contaminated soil and water (Table 1).

A bacterial consortium isolated from soil, involving four Alpha-*Proteobacteria* (*Agrobacterium tumefaciens*, *Caulobacter crescentus*, *Sphingomonas yaniokuyae*,

Table 1 List of prokaryotic organisms capable of degrading various triazine herbicides

	Name	Target triazine	References
α-Proteobacteria	*Agrobacterium* sp.	Atrazine; ametryn; cyanazine; prometon; simazine	[61]
	Agrobacterium radiobacter J14a	Atrazine (as the sole nitrogen source)	[62]
	Acinetobacter iwoffii	Simazine	[63]
	Chelatobacter heintzii (*Aminobacter aminovorans*)	Atrazine	[64]
	Ochrobactrum oryzae	Atrazine (in a semi-salinity media)	[65]
	Pseudaminobacter sp.	Atrazine	[66]
	Rhizobium sp.	Atrazine; simazine	[67, 68]
	Sinorhizobium sp.	Atrazine	[61]
β-Proteobacteria	*Achromobacter sp.*	Atrazine	[69]
	Advenella incenata	Terbuthylazine	[49]
	Janthinobacterium lividum	Terbuthylazine	[49]
	Burkholderia sp	Simazine	[63]
	Delftia sp.	Atrazine	[70]
	Polaromonas sp.	Atrazine	[61]
	Ralstonia sp. M91-3	Atrazine	[71]
γ-Proteobacteria	*Acinetobacter* sp.	Atrazine; simazine	[72–74]
	Klebsiella variicola strain FH-1	Atrazine	[75]
	Klebsiella planticola strain DSZ	Simazine	[76]
	Klebsiella pneumonia	Desethyl-atrazine	[77]
	Moraxella (Branhamella) sp.	Simazine	[78]
	Pseudomonas sp. strain MHP41	Simazine	[79, 80]
	Pseudomonas sp.	Atrazine, prometryn, simazine	[79, 81, 82]
	Pseudomonas sp. strain ADP	Atrazine, terbuthylazine	[82, 83]
	Pseudomonas stutzeri strain Y2	Simazine	[84]
	Pseudomonas spp. strain DSM 93–99 (YAYA6)	Atrazine	[85]
	Pseudomonas fluorescens strains LMG 10141 and 10140	Atrazine	[86]
	Shewanella sp.	Atrazine	[87]

(continued)

Table 1 (continued)

	Name	Target triazine	References
Actinobacteria	*Arthrobacter* sp.	Atrazine, terbuthylazine	[88–90]
	Arthrobacter aurescens TC1	Atrazine, ametryn, atratone, cyanazine, prometryn, simazine	[91]
	Arthrobacter crystallopoietes	Atrazine	[92]
	Arthrobacter ureafaciens strain XMJ-Z01	Simazine	[93]
	Citricoccus sp.	Atrazine	[94]
	Clavibacter sp.	Atrazine	[95, 96]
	Leucobacter sp.	Prometryn	[97]
	Microbacterium sp.	Atrazine	[70]
	Micrococcus sp.	Atrazine	[70]
	Nocardioides sp.	Atrazine, ametryn, atraton	[66, 98, 99]
	Rhodococcus sp. strain MB-P1	Atrazine	[100]
	Rhodococcus sp.	Atrazine; cyanazine; propazine	[101]
	Rhodococcus strain TE1	Atrazine, propazine, simazine, cyanazine	[102, 103]
	Rhodococcus rhodochrous	Atrazine	[74]
	Rhodococcus strain B-30	Atrazine propazine, simazine	[104]
	Rhodococcus corallinus strain NRRLB-15444R	Deethylsimazine, desethyl-atrazine, chlorine and amine groups	[77]
	Rhodococcus corallinus strain 11	Atrazine, atrazine metabolites	[77]
	Rhodococcus erythropolis strain NI86/21	Atrazine	[77, 105]
	Rhodococcus corallines	Atrazine	[101]
	Streptomyces strain PS 1/5	Atrazine cyanazine, metribuzin, prometryn	[106]
	Rhodococcus wratislaviensis FPA1	Terbuthylazine, simazine, atrazine, 2-hydroxysimazine, deetylatrazine, isopropylmine or ethylamine	[58]
Bacilli (Firmicutes)	*Bacillus* sp.	Metribuzin; atrazine; prometryn	[107, 108]
Deinococci (Deinococcus-Thermus)	*Deinococcus* sp.	Atrazine	[70]

Rhizobium sp.), one Beta-*Proteobacteria* (*Variovorax paradoxus*), one *Flavobacteriia* (*Flavobacterium oryzihabitans*), one *Actinomycetia* (*Nocardia* sp.), and one Gamma-*Proteobacteria* (*Pseudomonas putida*), was able to mineralize atrazine. Each member of this consortium had the *atz*C gene, responsible for ring cleavage. Dechlorination of atrazine was carried out only by *Nocardia* sp., which contained the *trz*N gene. Following dechlorination, hydroxyatrazine was further degraded via two separate pathways. In one pathway *Nocardia* converted hydroxyatrazine to *N*-ethylammelide via an unidentified gene product. In the second pathway, hydroxyatrazine (metabolized by *Nocardia* sp.) was hydrolyzed to *N*-isopropylammelide by *Rhizobium* sp., which contained the *atz*B gene. This consortium was tested in a liquid media [109].

In another work five Gamma-*Proteobacteria* (*Pseudomonas alcaligenes*, *Pseudomonas putida, Pseudomonas syringae*, *Erwinia tracheiphila, Enterobacter agglomerans*), three Beta-*Proteobacteria* (*Acidovorax* sp., *Ralstonia eutrophus* and *Enterobacter agglomerans*) and one *Actinomycetia* (*Micrococcus varians*) were isolated from a soil [110]. The consortium was able to degrade 88% of atrazine (1,000 mg L^{-1}) in 10 days using the herbicide as the sole nitrogen source in a culture medium.

Some soil fungi (e.g., several *Aspergillus*, *Fusarium,* and *Penicillium*) can partially degrade triazines (Table 2), but they are not able to cleave the triazine ring. Fungi can perform an oxidative *N*-dealkylation of triazines and few species (e.g., *Penicillium luteum*) are able to form hydroxyl metabolites. Wood-degrading basid iomycetes are able to degrade atrazine due to their lignin-degrading system. The application of white-rot fungi to atrazine bioremediation appears promising, because they can tolerate a broad range of environmental conditions, including temperature, nutrients, and moisture contents [61].

All the microorganisms selected could be used for bioaugmentation purposes [56].

3 Bioremediation

The natural remediation capacity of a microbial community can be exploited and improved for bioremediation purposes. In fact, it has been demonstrated that natural microbial communities have a key role in triazine degradation. Since the number of aquifers which cannot be used for drinking purposes has been increasing due to triazine contamination, there is a need to investigate their natural biodegradation in soil and water and how to exploit this nature-based solution in bioremediation strategies. Soil or water bioremediation can be performed in situ (without soil excavation or water transportation, and the contaminants are treated on place), ex situ (if the contaminated soil is excavated, treated on site and returned to the original location).

Table 2 List of fungi capable of degrading various triazine herbicides

	Name	Target triazine	References
Eurotiomycetes (Ascomycota)	*Aspergillus fumigatus*	Atrazine, simazine	[111]
	Aspergillus flavipes	Atrazine	[111]
	Aspergillus ustus	Atrazine	[111]
	Aspergillus niger	Atrazine	[112]
	Aspergillus oryzae	Terbuthylazine	[113]
	Penicillium brevicompactum	Terbuthylazine	[113]
	Penicillium decumbens	Atrazine	[111]
	Penicillium janthinellum	Atrazine	[111]
	Penicillium luteum (*Ascospirella lutea*)	Atrazine	[111]
	Penicillium rugulosum (*Talaromyces rugulosus*)	Atrazine	[111]
	Penicillium steckii DS6F	Simazine	[78]
Sordariomycetes (Ascomycota)	*Metarhizium brunneum*	Ametryn	[114]
	Trichoderma viride	Atrazine	[111]
Saccharomycetes (Ascomycota)	*Pichia kudriavzevii* Atz-EN-01	Atrazine	[115]
	Saccharomyces cerevisiae	Atrazine	[116]
Leotiomycetes (Ascomycota)	*Oidiodendron griseum*	Atrazine	[117]
Agaricomycetes (Basidiomycota)	*Pleurotus pulmonarius*	Atrazine	[118, 119]
	Lentinula edodes	Terbuthylazine	[113]
	Phanerochaete chrysosporium	Atrazine	[120]
Boletales (Basidiomycota)	*Rhizopogon vinicolor*	Atrazine	[117]
Hysterangiales (Basidiomycota)	*Trappea darkeri*	Atrazine	[117]
Mucoromycetes (Mucoromycota)	*Rhizopus stolonifera*	Atrazine	[111]

The presence of bacteria able to degrade triazines has also been shown in groundwater, although at significantly longer disappearance times than surface water or soil [49].

3.1 Bioaugmentation

There are few works in which adding microbial strains to soil or groundwater improved degradation of triazines in field studies. Most works report triazine degradation in bioaugmentation studies in laboratory cultures [48]. Moreover, bioaugmentation tests with bacterial strains included degradation of high concentrations of herbicide. For example, Mandelbaum et al. [82] tested *Pseudomonas* sp. strain ADP for the degradation of >1,000 μg mL^{-1} of atrazine as the sole nitrogen source.

Struthers et al. [62] showed the capability of *Agrobacterium radiobacter* J14a to degrade 50–200 μg g^{-1} of atrazine with higher mineralization rates (from two to five times) than those obtained from a non-inoculated soil.

Inoculation of a loam soil with *Pseudomonas* sp. ADP, *Pseudaminobacter* sp. strains C147, C195 and C223, and *Nocardioides* sp. strain C190 increased atrazine mineralization (10 mg atrazine L^{-1}) in soil suspensions [121]. *Pseudaminobacter* and *Nocardioides* utilized atrazine as the sole carbon and nitrogen source, whereas the *Pseudomonas* used the herbicide as the only nitrogen source.

Although microbial free cells degrade triazines with high effectiveness under laboratory conditions, several aspects (e.g., competition with indigenous microbes, severe environmental conditions, and genome instability) can limit the survival and bioaugmentation efficiency during in situ remediation.

Recently studies where bacteria were immobilized on a support showed a significant improvement of survival, retention, and biodegradation rates of the strains bioaugmented. For example, Zhang et al. [84] found that, immobilizing on beads *Pseudomonas stutzeri* Y2 (isolated from a wastewater of a pesticide factory), it was able to degrade efficiently atrazine, simazine, and terbuthylazine in a soil. The authors established that the mixture for obtaining optimal beads consisted of 14% polyvinyl alcohol, 1–3% sodium alginate, 2% activated carbon, and 1–2% of bacterial strain cells. The immobilized strain was able to degrade 0.57–1.17 mg kg^{-1} of simazine with DT_{50} values of 17.2–12.4 days lower than the times obtained using the same bacteria as free cells ($DT_{50} = 22.9$–17.4 days).

Desitti et al. [122] tested for atrazine removal the *Pseudomonas* sp. ADP strain encapsulated in core-shell electrospun microtubes. A degradation of 83.1 ± 3.9% at 50 days of an initial atrazine concentration of 20 mg L^{-1} was found, without adding any external carbon source.

Pseudomonas sp. ADP was also tested by Pannier et al. [123] using a sol-gel process for immobilizing the degrading bacterial strain in thin silica layers coated onto water-retaining carrier materials; a removal of 94% of 20 mg L^{-1} atrazine was found with this new material. The strain was able to maintain a high atrazine degradation activity after 1 year.

Pseudomonas sp. strain MHP41 encapsulated in an alginate matrix [80] was able to promote simazine (about 10 or 100 mg kg^{-1} simazine, corresponding to 3.5 or 35 kg ha^{-1}, respectively) biodegradation in soil.

Kumar et al. [124] tested the biodegradation capabilities in soil of a bacterial consortium (composed by *Bacillus*, *Pseudomonas,* and *Burkholderia*) immobilized in sodium alginate. About 90% of an initial atrazine concentration of 10 mg g^{-1} soil was degraded at 6 days of incubation and only 0.3% of applied atrazine was observed at 10 days.

Other authors identified a consortium composed of four *Bacteria* (*Xanthobacter*, *Ralstonia*, *Comamonas*, *Variovorax*) and one *Archaea* (ammonium oxidizing *Archaea*) able to degrade completely atrazine intermediates into nitrates. The consortium was tested in a fixed bed biofilm reactor for the herbicide (20 mg L^{-1}) degradation [100].

Improved atrazine degradation in soil slurries (20 mg kg^{-1} of herbicide) and water (10 mg L^{-1} of herbicide) was found, bioaugmenting *Rhodococcus erythropolis* NI86/21 encapsulated in different types of beads (alginate, bentonite, powdered activated carbon and skimmed milk). However, the wet alginate-based beads resulted impractical for field application because of their poor cell viability during storage [105].

The atrazine degradable microorganism *Arthrobacter sp.* ZXY-2 was immobilized on *Aspergillus niger* Y3 pellets (using the fungus as a biocarrier). Biochar (obtained from maize straw) with an optimal dosage (0.006 g biochar for 0.3 g pellets with the bacterial strain ZXY-2) was used for reducing the mobility of pollutants and microorganisms. The self-immobilized biomixture removed 50 mg L^{-1} atrazine in 1 h in liquid media in flask-shaking test, which was 61% higher compared to pellets without biochar [125].

A removal of atrazine (500 and 1,000 mg L^{-1}) close to 100% was found for the fungus *Pichia kudriavzevii* Atz-EN-01 immobilized on clay brick particles and encapsulated in a PVA-SA matrix in batch and fed batch culture experiments [115].

The bionanomaterial composed by the fungus *Saccharomyces cerevisiae* and Fe_3O_4 nanoparticles encapsulated in a sodium alginate-polyvinyl alcohol matrix was tested for the atrazine removal from aqueous solutions. A 100% degradation of 2 mg L^{-1} of herbicide, used as the sole carbon source, was found [116].

3.2 Biostimulation

Biostimulation is a highly efficient, cost effective and eco-friendly remediation technique. It refers to the addition of limiting nutrients like phosphorus, nitrogen, oxygen, electron donors to polluted sites to enhance the natural occurring bacteria to degrade a hazardous and toxic contaminant, including an herbicide.

Nitrogen content in soil can modulate triazine degradation in different ways. This fact has been studied extensively for *Pseudomonas* sp. ADP. In the presence of ammonium, nitrate, or urea, this bacterial strain metabolizes atrazine slower than in their absence [33]. Dehghani et al. [126] found nitrogen inputs (ammonium nitrate or urea) decreased herbicide biodegradation of a bacterial consortium which used atrazine as a nitrogen source.

In other studies, simazine degradation (initial concentration: 1.5 mg kg^{-1}) was enhanced by urea presence (500 mg kg^{-1}), in terms of both a smaller half-life and a higher amount of the desethyl-simazine metabolite formed. In fact, a DT_{50} of 32 days was observed in urea presence, significantly lower than that its absence (39 days), [43, 52].

Organic amendments can differently affect triazine degradation. For example, the addition of organic residues can adsorb herbicide, hampering its availability for biodegradation. An increase in terbuthylazine sorption to soil was found for pine residues (5% w/w in an agricultural clay-loam soil). Pine residues hampered microbial degradation owing to its high terbuthylazine sorption capacity, decreasing the bioavailability of the herbicide. On the contrary, oak residues did not increase significantly the herbicide sorption and terbuthylazine degradation at initial concentration of 1.5 mg kg^{-1} [50].

On the other hand, organic amendments can be used for reducing triazine leaching from soil. For example, several organic residues (sheep manure, spent coffee grounds, composted pine bark and coir) were tested for this purpose. The organic amendments (and in particular sheep manure and spent coffee grounds) were effective in reducing atrazine, simazine, and terbuthylazine leaching in a low content OM (0.9%) soil. A decrease in soil herbicide concentrations in comparison with the un-amended soils was also found [127].

Compost and vermicompost of olive cake were also tested for bioremediating triazine-contaminated soil. These amendments were used to stimulate biodegradation of simazine or terbuthylazine (1.5 μg g^{-1} soil). The compost and vermicompost addition enhanced the biodegradation of triazines during the first week of incubation, however at the end of the degradation experiment (60 days) no significant differences between non-amended and amended soil were found [128].

A recent review [129] compared straw, compost, and biochar for their suitability as agricultural soil amendments for enhancing microbial communities and reducing pesticide mobility. The organic amendments effects can vary due to several aspects (e.g., type of soil, application rate, and production procedure of the organic material). Biochar was found to be the most effective in increasing the sorption capacity.

3.3 Phytoremediation

Phytoremediation is the use of herbaceous and woody plants for improving microbial degradation of contaminated environments. Phytoremediation is based on the fruitful interactions between roots and the rhizosphere microbial community [130]. Plants can support directly degradation and/or stabilizing contaminants at root level (phytostabilization). In some cases, contaminants can also enter in the plant tissue (roots or shoot). The advantage of phytoremediation technologies is the possibility to treat contaminated soil or water *on site* [131, 132], including pesticides [133]. Pesticide remediation by phytoremediation has been found by phytoaccumulation, phytotransformation, and rhizoremediation [133].

Phytotransformation can partially detoxify triazines [134]. Atrazine and simazine have been reported to be metabolized by plants by conjugation with glutathione. In the case of atrazine, plant metabolization can occur with a hydroxylation mediated by benzoxazinones, conjugation to glutathione (catalyzed by glutathione-s-transferases), and dealkylation mediated by cytochromes P450 [135], with formation of deethylated atrazine. In the case of simazine, metabolization occurs via dealkylation followed by metabolization to hydroxysimazine.

However, the effectiveness of phytoremediation in removal of triazines is hampered by their intrinsic toxic effects (they act on photosynthesis and glycogenesis, inhibiting the photosystem II) and depends on a plant capability to resist to its biocide effect and to form synergic interactions with microorganisms.

For example, the atrazine degrader *Arthrobacter ureafaciens* strain DnL1-1 was found to colonize plant roots of maize and alfalfa and this fact was considered promising for further tests with atrazine degradation in field studies [136].

Among herbaceous plants, *Lolium* species were found to be able to degrade atrazine in soil. *L. multiflorum* was able to germinate and grow in presence of 1 mg Kg^{-1} of atrazine, with a pesticide removal higher than the natural attenuation [137].

Maize (*Zea mays*) demonstrated an atrazine removal capacity, but with a high herbicide accumulation [138]. This fact can be of great concern, since maize is a cultivable species.

Epiphytic root bacteria (*Pseudomonas* strains) were isolated from the rhizoplanes of *Acorus calamus, Typha latifolia,* and *Phragmites kark.* Subsequently, the *Acorus calamus*-bacteria combination was shown to degrade atrazine (5–10 mg L^{-1}), from 91 to 87% in 15 days [139].

The *Funneliformis mosseae* arbuscular mycorrhizal fungi in cooperation with the *Canna indica* plant were able to degrade atrazine (0.5–15 mg L^{-1}) in water. In 21 days, 96% of atrazine removal was found, compared to 68% with phytoremediation alone [140].

Some plants are capable of translocating atrazine and degrading partially them; simazine was found to accumulate in aquatic plants such as *Myriophyllum aquaticum* and *Canna hybrids* [141]. Pesticide phytovolatilization from leaves is considered not very important [142].

The aquatic plants *Leersia oryzoides* and *Typha latifolia* were able to reduce atrazine contamination (45% and 35%, respectively) from an initial concentration of 20 μg L^{-1}, [143].

In sediments of lakes, abiotic factors such as pH have a critical role in promoting atrazine degradation. Alkaline sediments in the presence of *Potamogeton crispus* and *Myriophyllum spicatum* were found to enhance pesticide degradation (initial conc.: 2 mg atrazine kg^{-1} dry sediment), [144].

Atrazine degradation was also found to be promoted in presence of trees, such as poplars [145].

In recent years, electrokinetic-assisted phytoremediation technology has also been tested for enhancing phytoremediation of atrazine [138, 146]. In these tests, maize phytoremediation plus an electric current (with voltage gradients of 2 and 4 V cm^{-1}) was used. The combined technology significantly enhanced (by 20–30%) the total atrazine accumulation in plant tissues, because atrazine was mobilized by the electric current [147].

Other electrokinetic-assisted phytoremediation tests were carried out with ryegrass (*Lolium perenne* L.). The total atrazine removal (2 mg kg^{-1} of soil) by plant increased by 7%, with the help of low voltage gradients (1 V cm^{-1}, 6 and 24 h per day) [138].

3.4 Other Approaches for Triazines Removal

Zhang et al. [148] used a new engineering rice, which contained a novel metabolic enzyme glycosyltransferase (ARGT1) that had the capacity to transform atrazine (0.2–0.8 mg L^{-1}). When comparing with common rice, the new rice had a higher survival in the atrazine contaminated environment and it accumulated 10–43% less atrazine than that of the rice wild type. The enzymes involved in *N*-dealkylation seems to be the cytochrome P450 monooxygenases. This fact was studied in *Tulipa gesneriana* L. and *Lolium rigidum,* in which this cytochrome conferred also resistance to triazine herbicides [149].

Because the microsomes of mammalian livers contain several P450s involved in xenobiotic metabolism, the introduction of mammalian P450 genes into plants is used for creating transgenic plants (e.g., rice, potato, and *Arabidopsis* plants) with high tolerance to triazines or capability to degrade them. For example, *Solanum tuberosum* expressing mammalian CYP1A1 have atrazine-tolerance [150]. *Oryza sativa* (rice) expressing the human CYP1A1 have the capability to remediate atrazine and simazine [149, 151]. Simazine was also found to be degraded by the transgenic *Arabidopsis thaliana* plant [152].

4 Conclusions and Future Remarks

Bioremediation is a nature-based solution which relies on the use of natural organisms for soil and water decontamination, therefore the application of engineering species is excluded. Although some plants, able to resist to toxic triazine effects, can promote triazine degradation through their exudates, the main role in atrazine, simazine, and terbuthylazine removal is due to microorganisms (bacteria, *Archaea*, and fungi). Moreover, only Prokaryotes can perform the complete degradation pathways until their mineralization. Herbicide contamination of agricultural soil can be managed with risk mitigation measures. Using microcosm experiments the site-specific time of triazine degradation of an agricultural soil can be evaluated; if possible, a soil can be taken out of production for the time necessary of triazine biodegradation (natural attenuation). Alternatively, bacteria able to improve herbicide degradation can be bioaugmented. Finally, in the case of vulnerable areas or if site-specific characteristics make triazine very persistent in soil, less persistent and new herbicides can be used. Recently, natural phytotoxins offer opportunities for the development of both directly used natural compounds and synthetic herbicides with new target sites based on the structures of natural phytotoxins.

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