Applied Soil Ecology 147 (2020) 103356

Contents lists available at ScienceDirect

Applied Soil Ecology

journal homepage: www.elsevier.com/locate/apsoil

Review

Soil biological activity as an indicator of soil pollution with pesticides – A review

Elżbieta Wołejko[a,*], Agata Jabłońska-Trypuć[a], Urszula Wydro[a], Andrzej Butarewicz[a], Bożena Łozowicka[b]

[a] Bialystok University of Technology, Department of Chemistry, Biology and Biotechnology, Wiejska 45A Street, 15-351 Białystok, Poland
[b] Institute of Plant Protection – National Research Institute, Chełmońskiego 22 Street, 15-195, Białystok, Poland

ARTICLE INFO

Keywords:
Soil
Microorganisms
Enzymes
Pesticides
Bioindicator

ABSTRACT

So far, there have been hardly any studies offering a comprehensive view of biological activity in soil, with little scholarly attention paid to the influence of different pesticides and their metabolites. The impact of the pesticides on soil health is still a current and important problem, which requires constant monitoring. The present review summarizes the recent scientific reports regarding soil enzymes and activities of microorganisms as well as changes occurring in underground biochemistry under the influence of pesticides. It is difficult to interpret enzymatic and microbiological responses after the application of pesticides because of their structural diversity and variety of breakdown pathways.

Pesticides applied to soil tend to be a mixture of different active substances. That is why it is difficult to analyze their influence on soil biological activity. The present review attempts to discuss the activity of such compounds on microbial communities and soil enzymatic activity. It also investigates pesticides degradation in soil and prevention of their negative effects on soil biological activity.

1. Introduction

Soil, a natural environment for the growth and development of plants, consists of a mixture of organic and mineral components occurring in gaseous, aqueous and solid states. Genetically and environmentally, soils differ significantly, yet, they tend to perform the function of reservoirs of water and nutrients necessary for a suitable development of the plant root system and microorganisms (Ndiaye et al., 2000).

Soil has the capacity of retaining various pollutants, such as heavy metals, pesticides or PAHs (Polycyclic Aromatic Hydrocarbon), therefore, it functions as a pollution absorber. They contribute to the contamination of the food chain, which can also potentially threaten human health (Riffaldi et al., 2006). Pesticides are the most common contaminants among all xenobiotics in soil. Their status is conditioned by the rapid population growth in the past 50 years and a growing demand for high-quality food. To cope with this situation, agricultural producers very often introduce procedures with an extensive use of pesticides, which result in their increased accumulation in the surface layers of soil and persistence in the environment. As predicted by Oberemok et al. (2015), in 2050, the use of pesticides in agricultural will be 2.7 times greater than in 2000, which probably will cause an increasing danger to human health for future generations.

The pesticides constitute a diverse group of inorganic and organic chemicals. According to WHO, there are four classes of toxicity: extremely hazardous (Ia), highly hazardous (Ib), moderately hazardous (II) and slightly hazardous (III). Classes Ia and Ib, the most dangerous, comprise eighty six pesticides, from which five belong to herbicides, eight – to fungicides, fifty-one – to insecticides and twenty-two – to other groups of compounds used for eliminating plant pathogens (World Health Organization & International Programme on Chemical Safety, 2010).

The active substances of pesticides produce pollution in soil environment, affecting microorganisms living there. Thus, they may also interfere with the correct sequence of biochemical pathways in soil biogeochemical cycles (Verma et al., 2014). The most dangerous compounds in the environment belong to the group of organochlorine pesticides. These pesticides are semi-volatile and can volatilize from soil to the atmosphere to be transported by airstream to other places. That is why they generate a new contamination site such as water and soil, which affects metabolism of microorganisms dwelling there (León-Santiesteban and Rodríguez-Vázquez, 2017).

* Corresponding author.
E-mail address: e.wolejko@pb.edu.pl (E. Wołejko).

https://doi.org/10.1016/j.apsoil.2019.09.006
Received 19 July 2019; Accepted 10 September 2019
Available online 07 November 2019
0929-1393/

Microorganisms habitat, their activity and interactions with each other are interdependent and they may vary even within a small distance. The most important soil microorganisms are: bacteria, fungi, algae, protozoa and nematodes, because their metabolism is associated with the flow of energy and the circulation of elements in ecosystems (Cycoń and Piotrowska-Seget, 2016).

Enzymes activity and the amount of hormones produced by soil microorganisms are important indicators of soil quality and its health because of their immediate response to natural or anthropogenic changes in soil. The analysis of microorganisms distribution in soil environment is a key factor determining the optimal conditions for the crop development and productivity (Hu et al., 2014).

Apart from the influence on microorganisms, the accumulation of the pesticides significantly impacts soil enzymes, which are essential catalysts influencing the habitat of the microorganisms in soil (Jarvis, 2007; Łozowicka et al., 2016). The enzymes present in soil may have various sources and origins, one of which is decaying prokaryotic or eukaryotic cells. Furthermore, soil enzymes can be independent extracellular proteins secreted into soil by fungi and roots of plants (Datta et al., 2017). It is difficult to interpret enzymatic and microbiological responses after the application of pesticides, because of their structural diversity and variety of their breakdown pathways (Gianfreda and Rao, 2008). It should also be mentioned that pesticides applied to soil usually consist of a mixture of different chemical compounds. Therefore, it is difficult to analyze their influence on biological soil activity.

Although the biological activity in soil under the influence of pesticides is an important issue, it has been neglected in research studies. Relatively few works have been devoted to this problem so far. The present review is a comprehensive presentation of the studies discussing the state of art on the activity of soil enzymes and microorganisms.

The main goal of the review is to report on the current research studies on the activity of soil enzymes and microorganisms viewed as a biological indicator of soil pollution. The specific objectives are threefolds: first, to analyze the changes in underground biochemistry conditioned by pesticides; second, to explain the influence of such compounds on microbial communities and enzymatic activity in soil; third, to discuss pesticides degradation in soil and prevention of negative effects of pesticides on biological soil activity.

2. Influence of pesticides on biological soil activity

The soil matrix constitutes a complex and difficult research material, because it is characterized by various overlapping environmental parameters such as: temperature, pH, granulometric composition, oxidoreductive potential, the presence of metal cations and other ions, and in some cases also various organic substances (humic acids, pesticides, PAHs, PCBs – Polychlorinated Biphenyls, etc.). All the aforementioned factors affect the activity of microorganisms and soil enzymes. The pesticides, especially organochlorine pesticides, pose a serious environmental problem due to their long degradation time. They may form bounds with organic and inorganic compounds, which have cytotoxic effects both on higher organisms and on the microorganisms living there.

In soil, effective degradation of pesticides occurs when organisms are capable not only of metabolizing and degrading them, but also of surviving in the contaminated environment. The rate of degradation depends on different factors, e.g. physico-chemical properties of the residue, characteristics of soil, climatic factors (temperature, rainfall, and humidity), and on the number of microorganisms able to decompose pesticides. Table 1 shows the main groups of the pesticides, mechanisms of their actions as well as microorganisms with the ability to biodegradation and their interactions. As already discussed by Gianfreda and Rao (2010), pesticides in soil should have relatively high solubility, low persistence and relatively high bioavailability, which will enable them to degrade fairly fast. However, the degrading organism or the extracellular enzyme and the chemical substances should be located sufficiently close to each other in order to be able to interact; the environmental conditions in terms of temperature, pH and soil properties must allow for proliferation of the degrading organisms or catalytic action of the degrading enzymes (Verma et al., 2014; Gianfreda and Rao, 2010). If all these conditions are not met, pesticides are not degraded. They accumulate and persist in soil for a long time, influencing negatively both biological soil activity and enzyme soil activity.

In the last decades, researchers have effectively marked different classes of the pesticides in environment samples. Due to the complex nature of soil samples and chemical structure of the pesticide, several extraction procedures for monitoring pesticide residues in soil have been investigated, including solvent extraction, Soxhlet extraction, microwave-assisted solvent extraction (MASE), ultrasonic solvent extraction (USE), supercritical fluid extraction (SFE) and matrix solid phase dispersion (MSPD) (Santos-Delgado et al., 2000; Crespo-Corral et al., 2008; Kaczyński et al., 2016). Over recent the years, the QuEChERS method introduced by Anastassiades et al. (2003) has become an attractive alternative technique for the pesticide multiresidue analysis in solid matrices (Pinto et al., 2010; Mantzos et al., 2013; Peysson and Vulliet, 2013; Bolshakov et al., 2014).

Pesticides have been analyzed with various analytical methods such as capillary electrophoresis, high performance liquid chromatography coupled with UV detection and gas chromatography (GC) flame ionization detector (FID), with electroncapture detection (ECD) or nitrogen-phosphorus detection (NPD) (Łozowicka et al., 2017). Nowadays, for large-scale multi-class pesticides analyses, liquid chromatography (LC) and gas chromatography (GC) coupled with tandem mass spectrometry (MS/MS) are commonly used as basic, complementary techniques (Kaczyński, 2017).

Each pesticide is characterized by a half-life that depends on environmental conditions like moisture, temperature and soil type. Some pesticides may have a half-life shorter than 30 days, such as aldicarb (2–12 days), dicamba (15–24 days), cyanazine (2–5 days), captan (2–8 days), fenvalerate (19–29 days) (Cycoń and Piotrowska-Seget, 2016), and 2,4-D (1–14 days), and they are classified as non-persistent (Barraclough et al., 2005). Moreover, for other pesticides, this time is greater than 100 days, for instance, chlordane (93–154 days), terbacil (204–252 days), lindane (120 days), tebuthiuron (360 days) and bromacil (144–198 days), so they are persistent (Gianfreda and Rao, 2008; Barraclough et al., 2005). However, non-persistent pesticides may also be dangerous, because their degradation products are frequently transformed by microorganisms and they subsequently exhibit a different behavior from their parent compound. Such a situation was observed in the case of glyphosate (Sviridov et al., 2015).

2.1. Pesticides and microbiological activity in soil

Soil microorganisms play a key role in the circulation of elements and in the decomposition of organic matter residues, affecting the nutrient and carbon cycle (Mahdi et al., 2017). Their high activity is concentrated in the topsoil, the depth of which may vary from several centimeters to 30 cm. Moreover, microorganisms contribute to the transformation and degradation of waste materials and synthetic organic compounds. They also influence the physical properties of soil (Riffaldi et al., 2006). Therefore, microorganisms may function as an excellent indicator of soil health change, thereby providing an early sign of soil quality improvement or an early warning of soil degradation (Mahdi et al., 2017).

Interestingly, the microorganisms exposed to pollution produce mechanisms enabling their adaptation to the prevailing conditions, which is corroborated by the studies on bacterial enzymes conducted by Sun et al. (2004). This activity is thought to have evolved, so that microorganism would take advantage of the active substance of the pesticides in soil environment. According to Webber et al. (2015), the

Table 1
Microorganisms degrading various group of pesticides and their interactions.

Pesticides type	Pesticide chemical group	Pesticide properties	Microorganisms	Examples of interactions between pesticides and microorganisms	Ref.
Insecticides	Benzoylurea	Selective, acts by inhibiting chitin synthesis, inhibitor of chitin biosynthesis, type O.	*Paracoccus* sp., *Pseudomonas sp.,*	- Diflubenzuron, flufenoxuron and novaluron suppresses microorganisms in acidic loam soil.	Mommaerts et al., 2006 Hsiao et al., 2013
	Carbamates	Carbamate acid derivatives, kill a limited spectrum of insects, highly toxic to vertebrates, relatively low persistence	*Pseudomonas sp., Flavobacterium, Achromobacterium, Sphingomonas, Bacillus pumilus SE34, Arthrobacter, Stenotrophomonas maltophilia M1*	- Carbofuran increases soil microbial population or causes no significant change in total viable amount of bacteria.	Kim et al., 2004 Sarnaik et al., 2006 Mohamed, 2009
	Neonicotinoid	Systemic with translaminar activity, contact action affecting insects nervous system, no long term activity, acetylcholine receptor (nAChR) agonist.	*Pseudomonas* sp., *Bacillus subtilis* FZB24, *Bacillus amyloliquefaciens* IN937a, *Bacillus pumilus* SE34, *Rhizobium* sp.	- Thiamethoxam and imidacloprid cause no significant change in total viable amount of bacteria.	Myresiotis et al., 2012 Ahemad and Khan, 2011 Sarnaik et al., 2006
	Organochlorines	Soluble in lipids, accumulate in fatty tissue of animals, transferred through the food chain, toxic to a variety of animals, long-term persistent	*Mycobacterium sp., Arthrobacter sp., Aerobacter Aerogenes, Sphingobium sp., Xanthobacter autotrophicu, Pseudomonas fluorescens, Phaseolus vulgaris*	- HCH increases soil microbial population. - Lindane and endosulfan affectes cell morphology which result in a large number of pleomorphic cells.	Fenlon et al., 2007 Erick et al., 2006 Das and Mukherjee, 2000
	Organophosphates	Soluble not only in organic solvents, but also in water, infiltrate reaching groundwater, less persistent than chlorinated hydrocarbons, some affect the central nervous system, absorbed by plants, transferred to leaves and stems - the supply of leaf-eating insects	*Pseudomonas diminuta, Pseudomonas aeruginosa, Burkholderia cepaeia* Serratia ficaria, Yersinia enterocolitica	- Diazinon inhibites the growth *of Proteus vulgaris*, a urease-producing bacterium. - Phorate, chlorpyrifos and monocrotophos cause no significant change in total viable amount of bacteria. - Chlorpyrifos affects cell morphology and resulted in a large number of pleomorphic cells. - Methamidophos and profenofos decreases microbial biomass (41–83%) after the use of. - Ethion adversely affects soil microorganisms. - Phorate decreases total number of bacteria and N2-fixing bacteria, while malathion increases denitrifying bacteria. Nitrifying and fungal populations were not affected.	Fenlon et al., 2007 Wang et al., 2006 Sarnaik et al. (2006) Gonzalez-Lopez et al., 1993
	Pyrethroids	Affect the nervous system, less persistent than other pesticides, the safest in terms of their use, some used as household insecticides	*Achromobacter, Acidomonas, Bacillus, Brevibacterium, Catellibacterium, Clostridium, Lysinibacillus, Micrococcus, Ochrobactrum, Pseudomonas, Serratia, Sphingobium, Streptomyces, Aspergillus, Candida, Cladosporium, and Trichoderma,*	- Cypermethrin stimulates dehydrogenase when applied singly, but inhibits in combination with other pesticide.	Cycoń and Piotrowska-Seget, 2016 Gundi et al., 2007
Fungicides	Benzimidazole	Systemic Activated Resistance (SAR), induces host plant defense and inhibition of mitosis and cell division.	*Bacillus pumilus* SE34, *Rhodococcus qingshengii* sp., *Rhodococcus jialingiae* sp.	- Carbendazim reduces soil microorganisms	Myresiotis et al., 2012 Wang et al., 2010
	Carbamate	Systemic with protective, curative and eradicative action, cellulose and lipid synthesis inhibitor.	*Bacillus sp.*	- Thiram reduces soil microorganisms. - Carbofuran stimulates the population of *Azospirillum* and other anaerobic nitrogen fixers in soil.	Myresiotis et al., 2012 Niewiadomska, 2004
	Carboxamide	Protectant, foliar absorption, translocates, inhibits spore germination and germ tube elongation, Succinate Dehydrogenase Inhibitor.	*Rhodospirillum* sp., *Aspergillus* sp., *Penicillium* sp.	- Disruption of the electron respiration chain in microbial cells by boscalid	Miyamoto et al., 2009 Yang et al., 2012
	Phenylamide	Systemic with curative and protective action, acts by suppressing sporangial formation, mycelial growth and the establishment of new infectons. Disrupts fungal nucleic acid synthesis - RNA ploymerase 1	*Pseudomonas fluorescens* and *Chrysobacterium indologenes*	- Metalaxyl applications influences negatively the microbial population.	Monkiedje and Spiteller, 2005
	Strobilurin	Protectant, curative and translaminar, respiration inhibitor QoL-fungicide (Quinone outside Inhibitors).	*Bacillus cereus, Azotobacter* sp, *Bacillus subtilis* B19	- Azoxystrobin cause no significant change in total viable amount of bacteria.	Verma et al., 2014
	Triazole	Systemic with curative and protective action, inhibits the demethylation of steroids distrupting ergosterol biosynthesis, disrupts membrane function.	*Streptomyces* sp., *Serratia* sp, *Pseudomonas fluorescens*	- Hexaconazole adversely affects soil microorganisms. - Tebuconazole cause no significant change in total viable amount of bacteria.	Eizuka et al., 2003 Santacruz et al., 2005 Kalam and Mukherjee, 2001

(*continued on next page*)

Table 1 (*continued*)

Pesticides type	Pesticide chemical group	Pesticide properties	Microorganisms	Examples of interactions between pesticides and microorganisms	Ref.
Herbicides	Aryloxyphenoxypropionate	Systemic, absorbed through leaves and translocated, an acetyl CoA carboxylase inhibitor and inhibits fatty acid synthesis (ACCase).	*Pseudomonas azotoformans* QDZ-1, *Proteobacteria* and *Bacteroidetes*	- Microbial biomass, carbon and nitrogen were increased significantly in the fenoxaprop treated soils as compared to control.	Nie et al., 2011 Das et al., 2012
	Alkylchlorophenoxy	Selective, systemic, absorbed through roots and increases biosynthesis and production of ethylene causing uncontrolled cell division and so damages vascular tissue, synthetic auxin.	Pseudomonas putida, Flavobacterium, Ralstonia eutropha, Burkholderia cepacia,	- 2,4-D inhibits the growth of *Rhizobium* sp. or 2,4-D stimulats anaerobic N-fixing bacteria.	Verma et al., 2014
	Diphenyl ether	Induces the accumulation of tetrapyroles which attack plant cells, inhibition of protoporphyrinogen oxidase (PPO).	*Pestalotiopsis* sp., *Cunninghamella echinulata, Trichosporon domesticum, Cryptococcus curvatus*	- Stimulatory effect of oxyfluorfen on the growth of non-symbiotic N2- fixing bacteria in clay soil treated with NPK fertilizers.	Schauer and Borriss, 2004
	Chloroacetamide	Selective, inhibition of cell division and fatty acid	*Sphingobium quisquiliarum DC-2, Sphingobium baderi DE-13, Mycobacterium fortuitum, Bacillus cereus, Microbacterium sp., Gordonia polyisoprenivorans, Microbacteriaceae bacterium*	- Stimulated anaerobic fermentative and sulfate-reducing bacteria while inhibited acetogenic bacteria in paddy soil after the use of butachlor.	Li et al., 2013 Patnaik et al., 1996
	Hydroxybenzonitrile	Selective, systemic with contact action, acts by inhibiting photosynthesis at Photosystem II.	*Comamonas* sp. 7D-2, *Sphingopyxis* sp. OB-3	- Bromoxynil dies not influence (except for a short-termed stimulation of the number of bacteria) the amount and composition of the basic groups of soil microorganisms.	Chen et al., 2013 Abbas et al., 2014
	Organochlorine	Selective, absorbed by leaves and roots. Inhibits protoporphyrinogen oxidase (PROTOX), leading to irreversible cell membrane damage.	*Lysinibacillus* sp. ZB-1, *Pseudomonas zeshuii* BY-1, *Brevundimonas* sp. LY-2, *Flavobacteriaceae, Pseudomonadaceae, Sphingobacteriacea*	- Stimulation of indigenous pentachlorophenol bacterial degraders	Feng et al., 2012
	Phosphonoglycine	Broad-spectrum, systemic, contact action translocated and non-residual, inhibition of EPSP synthase.	*Arthrobacter* sp, *Achromobacter* sp., *Streptomyces* sp., Pseudomonas aeruginosa Bacillus megaterium	- Glyphosate produces a non-specific, short-term stimulation of bacteria.	Sviridov et al., 2015 Al-Arfaj et al., 2013 Ratcliff et al., 2006
	Sulfonylurea	Inhibits plant amino acid synthesis - acetohydroxyacid synthase AHAS	*Pseudomonas* sp. LW3, *Pseudomonas aeruginosa* L36, *Ancylobacter* sp. XJ-412-1, *Actinobacteria* sp., *Ochrobactrum* sp., *Candida mengyuniae* sp.	- Metsulfuron-methyl inhibits heterotrophic S-oxidizing and S-reducing bacteria but increases fungi. - Reduction of the growth of fluorescent *Psendomonads* - sulfosulfuron adversely affectes *Bradyrhizobium* sp. - Bensulfuron methyl decreases microbial biomass-C, and N.	He et al., 2006 Khan et al., 2006 Huang et al., 2010 Zhao et al., 2015; Arabet et al., 2014 Boldt and Jacobsen, 1998
	Triazine	Selective, systemic action with residual and foliar activity, inhibits photosynthesis (photosystem II).	*Arthrobacter nicotinovorans, Cryptococcus laurentii, Raoultella planticola, Phanerochaete chrysosporium*	- Atrazine adversely affects *Bradyrhizobium* sp. - Simazine and prometryn decreases total nitrogenase activity.	Khan et al., 2006 Swissa et al., 2014
	Triketone	Selective, absorbed by roots and translocated. Bleaching: inhibition of 4-hydroxyphenyl-pyruvate-dioxygenase.	Bradyrhizobium sp. SR1, Pseudomonas putida, Bacillus sp. Mes 11	- Mesotrion increases soil microbial population.	Romdhane et al., 2016
	Uracil	Inhibitor of protoporphyrinogen oxidase, non-selective, contact action absorbed by foliage. Inhibits photosynthesis (photosystem II).	*Psuedomans* spp.	- Bromacil reduces microbial biomass significantly for up to eleven months after application.	El-Nahhal and El-Hams, 2017
	Urea	Photosynthetic electron transport inhibitor at the photosystem II, sective, absorbed via roots and translocated	*Helianthus tuberosus, Aspergillus niger, Sphingomonas sp.* SRS2, *Variovorax paradoxus, Bacillus sphaericus, Delftia acidovorans, Pseudomonas sp., Cunninghamella elegans, Mortierella isabellina, Talaromyces wortmanii, Rhizopus japonicus, Rhizoctonia solani and Aspergillus niger*	- Isoproturon adversely affects *Bradyrhizobium* sp. - Isoproturon increases bacterial count and decreases actinomycetes and fungi. - 16S rRNA-PCR DGGE showed that isoproturon degradation was associated with proliferation of *Sphingomonas* spp.	Khan et al., 2006 Wang et al., 2010 Sørensen et al., 2003 Bending and Rodrıguez-Cruz, 2007

processes causing the emergence and maintenance of pesticide-resistant bacteria are mainly triggered by abusive and continuous pesticide use, which influences most bacterial species, so that they acquire resistance through single, continuous or spontaneous mutations. It leads to the acquisition of new genes by allowing for overproduction of enzymes that break down pesticides, antibiotics and other toxic compounds (Rangasamy et al., 2018). Moreover, the combination of pesticides with fertilizers may also influence microbial diversity and activity in soil environment. Lin et al. (2011) and Chen et al. (2001) reached similar conclusions when they analyzed the mutual influence of inorganic fertilizers, pesticides and heavy metals on the microbial activity.

In soil, various biochemical and physiochemical transformations of pesticides produce different metabolites. Some of them do not have any effect on microorganisms, whereas other can be lethal. In most cases, applying the pesticides destroys certain microorganisms, subsequently creating niches inhabited by other microorganisms. The research study by Chen et al. (2001) confirmed that applications of fungicides such as benomyl, captan and chlorothalonil destroyed or inhibited the activity of certain fungi in soil, which led to a rapid flush of bacterial activity. Pal et al. (2008) also observed a reduction in the number of non-pathogenic saprophytic soil fungi in the case of fungicides, such as pencycuron, dithianon or prochloraz introduced into soil (Tejada et al., 2011). In turn, the reduction of microorganisms biomass was observed after the application of tebuconazole and pencycuron used to protect rice crops (Muñoz-Leoz et al., 2011). In addition, as noted by White et al. (2010), the introduction of chlorothalonil fungicide to soil increased the stability of some herbicides in the soil – fourfold in the case of isoproturon and twofold in the case of metalchlorol (White et al., 2010).

It should also be mentioned that herbicides cause the disturbance of bacterial metabolism, which results in a decrease in soil enzymatic activity and the disruption of biological binding of nitrogen (Singh, 2016). The addition of herbicides, like Roundup, periodically inhibits the development of non-symbiotic diazotrophs up to 30 days after their introduction into soil environment. For example, during the degradation of glyphosate (Fig. 1), some bacteria, like *Arthrobacter* sp, *Achromobacter* sp., *Streptomyces* sp., can use degradation products such as nitrogen, phosphorus and carbon for their growth and activity (Sviridov et al., 2015).

During its metabolism in soil, a pesticide is initially transformed by oxidation, reduction or hydrolysis to a more water-soluble form. Next, the pesticide or pesticide metabolite is combined with an amino acid or sugar, which increases its water solubility. At the final stage, it is transformed into secondary conjugates that are non-toxic (Van Eerd et al., 2003). Table 1 shows that many studies reported both negative and positive effects of pesticides on soil microbial biomass and soil microorganisms. This state of affairs may be related to the fact that after introducing a new substance into the environment, the response of microorganisms is immediate, which tends to result in a decrease in the activity of enzymes and microorganisms (Widenfalk et al., 2008). In turn, a repeated introduction of a given plant protection product into the environment fosters the adaptation of microorganisms to this pesticide. The lack of reaction of soil microorganisms observed on re-applying a given pesticide may be related to the development of the ability of soil microorganisms to accelerate the degradation of a given agent or the acquired tolerance of microorganisms to the pesticide (Mele and Crowley, 2008). Although the conducted research study indicated a high toxicity of the test compound relative to a specific strain or group of microorganisms, its introduction into the environment may not have a significant impact on the functioning of the ecosystem. This is the case when other microorganisms take on the physiological role of those which due to contamination with pesticides have fallen out of the soil microbiome (Tejada et al., 2011; Pal et al., 2008).

Moreover, it should be pointed out that once pesticides are released into the environment, their structure becomes strongly related to soil microbiological composition, enzymes bound to soil colloids and humic substances (Gundi et al., 2007). Some experimental studies have also shown significant influence of soil pH on a bacterial community in soil. Hsiao et al. (2013) stated that the dissipation rate of insecticides was higher in an alkaline sandy loam soil, so the bacterial communities in this soil were more homogenous than in an acidic loam soil.

In the course of pesticide degradation, depending on the type of bacteria, the degradation of the pesticides may follow different pathways, which results in the formation of varied metabolites (Cycoń and Piotrowska-Seget, 2016), as shown in Table 2. For example, the degradation of fenpropathrin by *Bacillus cereus* ZH-3 initially produced α-

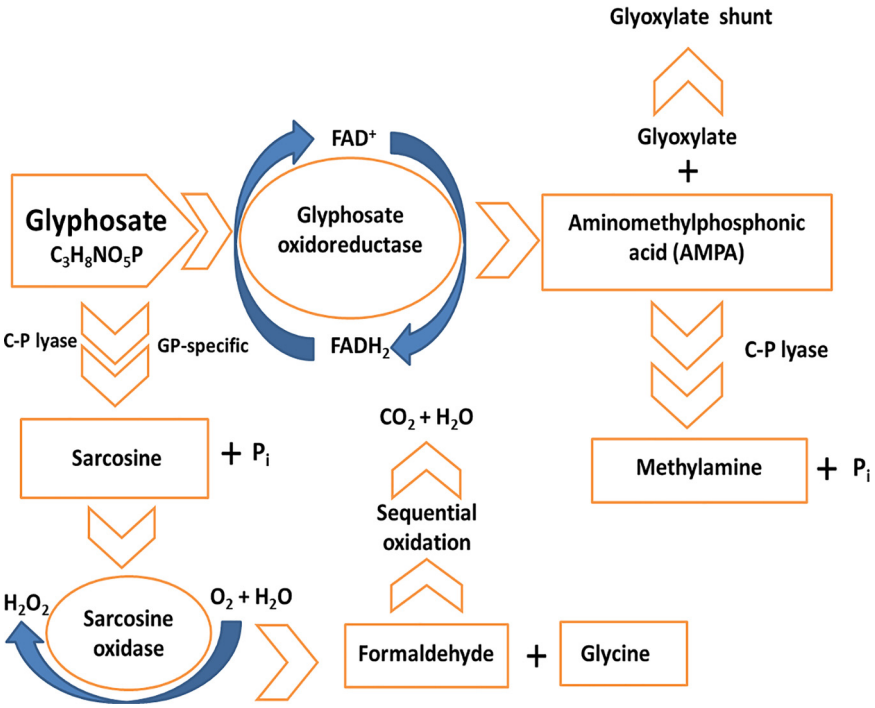
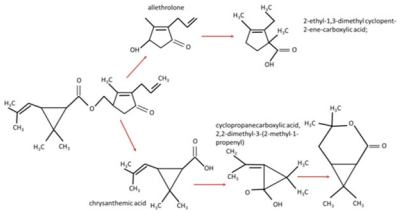
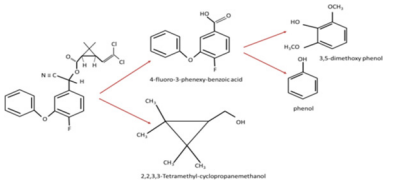
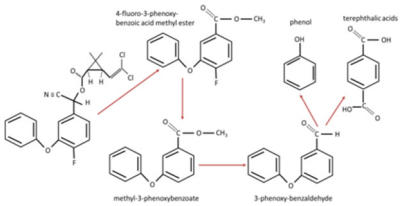
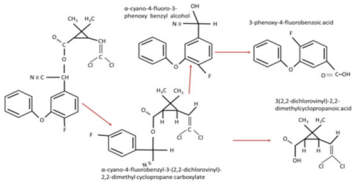
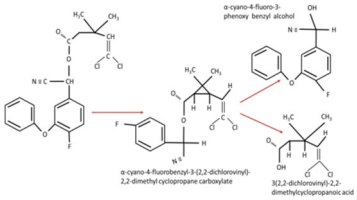
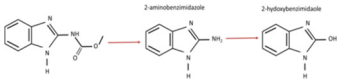
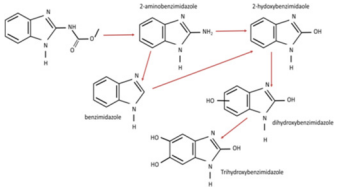
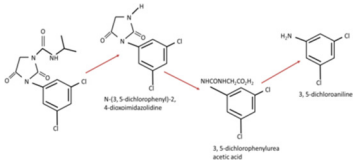
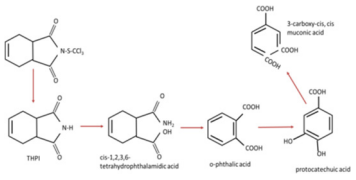


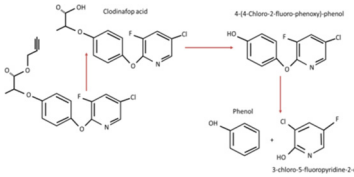
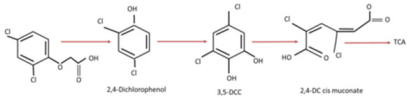
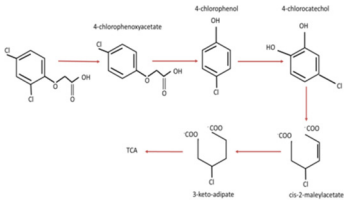
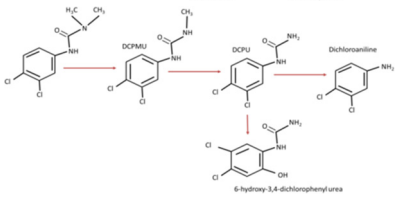
Fig. 1. Microbial degradation of glyphosate via AMPA and via sarcosine (Sviridov et al., 2015).

Table 2
Metabolites and various degradation pathways of pesticides depending on the type of microorganisms.

Pesticides	DT_{50}	Microorganisms	Metabolites and proposed pathways for degradation	Ref.
Allethrin (I)	60 days	*Acidomonas* sp.		Paingankar et al., 2005
Cyfluthrin (I)	33 days	*Br evibacterium aureum* DG-12		Chen et al., 2013
		Lysinibacillus sphaericus FLQ-11-1		Hu et al., 2014
β-Cyfluthrin (I)	13 days	*Pseudomonas stutzeri* S1		Saikia et al., 2005
		Trichoderma viridae (5-2)		Saikia and Gopal, 2004
Carbendazim (F)	20-40 days	*Bacillus licheniformis* JTC-3		Panda et al., 2018
		Mycobacterium sp. SD-4		Zhang et al., 2017
Iprodione (F)	13.4-36.2 days	*Arthrobacter* sp. MA6 *Microbacterium* sp.		Mercadier et al., 1997
Captan (H)	0.8-3.7 days	*Bacillus circulans*		Megadi et al., 2010

(*continued on next page*)

Table 2 (*continued*)

Pesticides	DT_{50}	Microorganisms	Metabolites and proposed pathways for degradation	Ref.
Clodinafop propargyl (H)	0.7-1.5 days	*Pseudomonas* sp. strain B2		Singh and Singh, 2016
2,4-D (H)	4.4-28 days	*Pseudomonas* sp.		Singh and Singh, 2016
		Azotobacter chroococcum		Kumar et al., 2014
Diuron (H)	146.6- 229 days	*Beauveria bassiana, Caenorhabditis elegans, Phanerochaete chrysosporium*		Singh and Singh, 2016

I-insecticide; F-fungicide; H- herbicide; DT50 - values (time required for 50% dissipation of the initial concentration) according by PPDB, 2019.

hydroxy-3-phenoxy-benzenacetonitrile. It was transformed into 3-phenoxybenzenaldehyde, and, in the final stage, phenol was generated (Liu et al., 2015). During fenpropathrin degradation by *Ochrobactrum tritici* pyd-1, the initial products were cyano-3-phenoxybenzylalcohol and 2,2,3,3-tetramethyl cyclopropanecarboxylic acid. In the next stage, the latter product was transformed into 3-phenoxybenzaldehyde, which turned into 3-phenoxybenzoic acid. The cleavage of 3-phenoxybenzoic acid resulted in the formation of protocatechuate and 4-hydroxy-3-phenoxybenzoic acid. Next, the acid was transformed into p-hydroquinone, which in the final stage was transformed into 3-oxoadipate (Wang et al., 2011). Metabolites detected during the degradation of fenpropathrin by *Pseudomonas aeruginosa* were similar to those produced during the degradation by *Bacillus cereus* ZH-3, but in the final stage, 3-phenoxybenzoic acid arose (Song et al., 2015).

Furthermore, the degradation pathways of cypermethrin are also different, depending on various groups of microorganisms which decompose the above mentioned pesticide. During its degradation by *Bacillus* sp. ISTDS2, cypermethrin could be metabolized into two compounds: 3-(2, 2-dichloroethenyl)-2,2-dimethyl cyclopropanecarboxylate and α-hydroxy-3-phenoxy-benzene acetonitrile. The latter product is unstable and may be spontaneously transformed to yield 3-phenoxy benzaldehyde. Chen et al. (2011) reported that 3-phenoxy benzaldehyde has antimicrobial activity, but it does not affect the growth of microorganisms. It enhances biodegradation in soil and when metabolized by *Bacillus* sp. SG2, it is transformed into 4-hydroxybenzoate. It converts to 4-propylbenzaldehyde, next, to phenoxy benzoic acid, then, phenyl ester of o-phenoxy benzoic acid arises and, in the final stage – phenol. As observed by Bhatt et al. (2016), *Bacillus* sp. SG2 was able to degrade complete cypermethrin. Therefore, it can be an ideal microorganism for bioremediation of cypermethrin in the contaminated soil.

According to the literature, individual strains of bacteria or fungi can break down the active substance of a pesticide, however, this process is slower than in the case of a microorganisms consortium. This is due to the fact that a consortium can contain various strains of bacteria and fungi. They may become active at various stages of decomposition and can use pesticide degradation products, contributing to the faster degradation of pesticides (Das and Varma, 2011). As noted in the studies by Sasikala et al. (2012), after 21 days of incubation, a microorganisms consortium consisting of *Bacillus cereus, Pseudomonas aeruginosa, Serratia marscecens* and *Klebsiella* sp. was able to degrade approx. 65.87% chlorpyrifos and to forme 3,5,6-trichloro-2-pyridinol in soil. In addition, the research study conducted by Zhu et al. (2017) showed that after 7 days the degradation efficiency of atrazine in soil by two strain *B. licheniformis* ATLJ-5 and *B. megaterium* ATLJ-11 can reach approx. 99% of atrazine degradation. Table 2 presents several examples of the consortia participating in the decomposition of pesticides such as Iprodione and Diuron. As discussed by Mercadier et al. (1997), during the first stage, Iprodione is decomposed by three types of strains such as *Pseudomonas* sp., *Pseudomonas fluorescens* and *Arthrobacter*. In subsequent stages, one more strain *Pseudomonas paucimobilis*, which does not take part in the first stages of the decomposition, degrades Iprodione forming a consortium together with the three strains. In the last stage, this strain, i.e. *Pseudomonas paucimobilis,* allows for the decomposition of 3,5-dichlorophenylurea acetic acid to 3,5-dichloroaniline, glycine and CO_2.

2.2. Pesticides and enzymatic activity of soil

The rate of enzymatic reactions in soil fluctuates with seasons and it is determined mainly by the concentration of enzymes and substrates participating in the reactions, influenced especially by pH, granulometric composition, temperature and the presence of activators and inhibitors (Gianfreda and Rao, 2010; Jian et al., 2016). Soil enzymes enter humus–enzyme complexes, changing their kinetic properties and resistance to thermal denaturation and proteolytic degradation (Gianfreda and Rao, 2010). However, the stability of the enzymes in soil depends on the binding mode, the number and type of chemical bonds between the enzyme and the sorbent, the chemical and physical properties of the sorbent phase, the changes in the molecular conformation of the enzyme and the chemical conditions of the microenvironment surroundings (Nannipieri et al., 2012). As discussed by

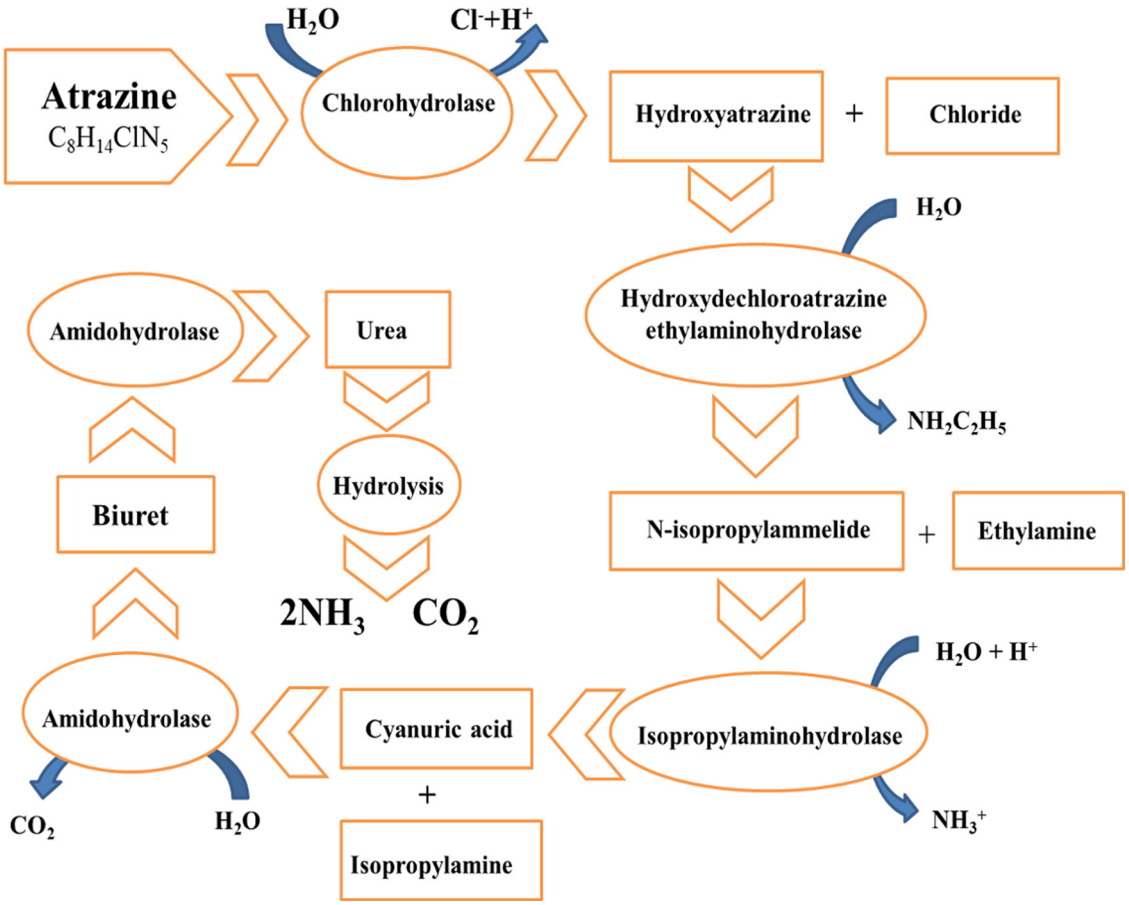


Fig. 2. Pathway enzymatic degradation of atrazine in soil (Lin et al., 2011).

Gianfreda and Rao (2010), adsorption of the enzymes onto clay minerals can make the immobilized enzyme more resistant to denaturation. However, it is of minor importance in the case of enzyme adsorption on humus substances, because entrapment of the enzyme in the humic substances stabilizes the enzymes molecule. Yet, it does not influence their resistance to denaturation after the application of organic and inorganic substrates.

According to Gianfreda and Ruggiero (2006), the loam soil may protect enzymes against the inhibitory effect of certain pesticides, such as carbaryl and atrazine. It was confirmed by the fact that phosphatases immobilised on montmorillonite were less affected by these pesticides than the free and organo- and organo-mineral-complexed phosphatases. In addition, the study by Fenlon et al. (2007) also described the negative influence of pesticides on the enzyme and on the activity of microbial population. For instance, some insecticides, like quinalphos, monocrotophos, and cypermethrin, at the highest concentrations in single and/or combination doses reduce the activity of dehydrogenases, while these pesticides in lower concentrations stimulate their activity (Gundi et al., 2007). Fragoeiro and Magan (2008) demonstrated that the use of trifluralina, dieldrin and simazine reduces the activity of dehydrogenases in soil, while diazinon stimulates their activity (Fenlon et al., 2007). In turn, the use of fenamiphos, an organophosphate insecticide, at a dose of up to 5 kg ha^{-1} does not affect dehydrogenases in the soil environment (Hussain et al., 2009). The research study conducted by Cai et al. (2007) shows that a herbicide called acetochlor [2-chloro-N- (ethoxymethyl) -N- (2-ethyl-6-methylphenyl) acetamide] in an amount of 10–100 mg kg^{-1} has no reducing effect on dehydrogenases, only a dose above 250 mg kg^{-1} causes up to 60% inhibition of the activity. The application of herbicides S-metolachlor and mesotrione at the recommended doses in single or combination results in an increase of dehydrogenases activity. With the disappearance of the pesticide active substance in soil, dehydrogenases activity also decreases (Wołejko et al., 2017). According to Dilly and Nannipieri (2001), the activity of enzymes may be induced or repressed by the presence of particular compounds without a change in microbial biomass. Cycoń et al. (2010) reported that these discrepancies in studies can be associated with differences in soil properties and the composition of microbial population.

In addition, Yun et al. (2006) showed that after the chlorothalonil application, there is a decrease in the activity of alkaline and acidic phosphatases, catalase and urease in soil. Moreover, as reported by Wyszkowska et al. (2008), the activity of dehydrogenases and urease significantly decreases, but alkaline phosphatase activity increases after the application of herbicide (Apyros 75 WG). Sviridov et al. (2015) reported that after the addition of glyphosate into soil, its positive influence on the activities of urease is observed, while the effect for phosphatases is inhibited. Furthermore, as suggested by Pizzul et al. (2009), in the presence of glyphosate in soil, there was an increase in the activity of ligninolytic enzymes, manganese peroxidase or laccase, which influence the rate of glyphosate decomposition.

Apart from enzymes in soil, as reported by Bertrand et al. (2015), the degradation of glyphosate into aminomethylphosphonic acid and glyoxylate is conducted by dehydrogenases operating with flavoprotein as a cofactor. It brings about the incorporation of one atom of oxygen on the substrate, while the other atom reacts with the electrons as a cofactor in the presence of NAD(P)H as a donor to form H_2O. Enzymes of the same class, like monooxygenases and dioxygenases, are involved in the degradation of aromatic rings which are often the basic structure of pesticides (Al-Arfaj et al., 2013). These enzymes are key players in the degradation of natural polymers that constitute soil organic matter. Moreover, microorganisms also produce other oxidative enzymes, such as peroxidase, laccase, and tyrosinase, that catalyze very specific

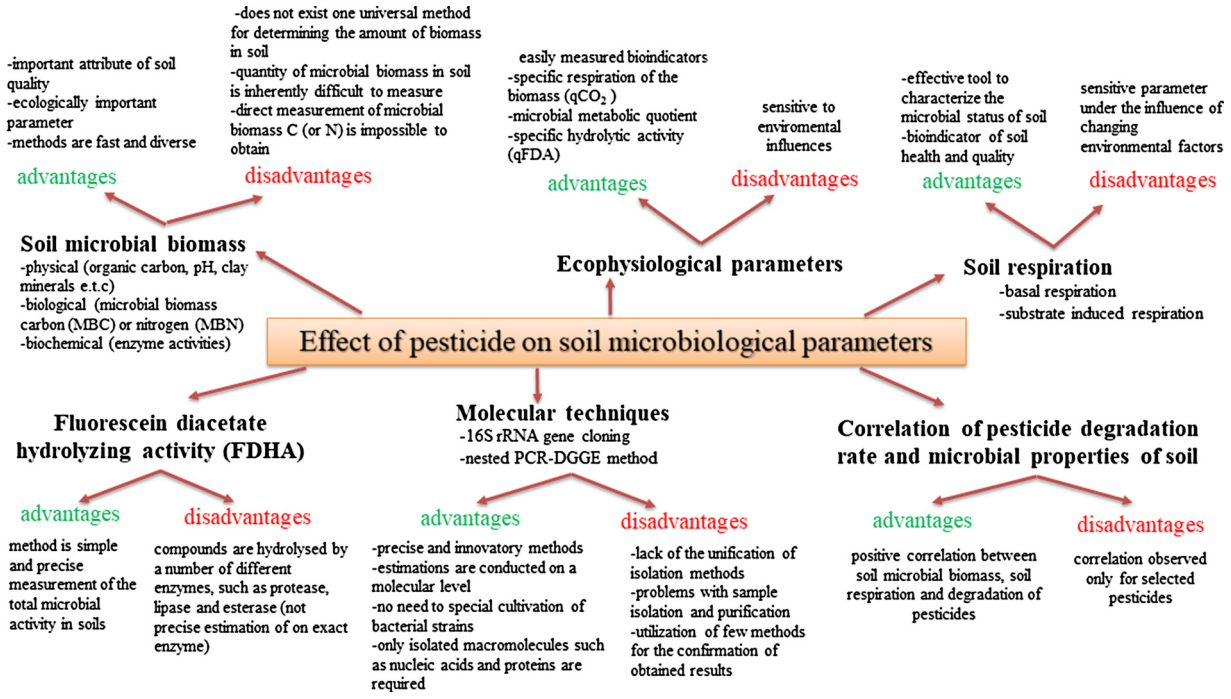


Fig. 3. Effect of pesticide on soil microbiological parameters (Chowdhury et al., 2008).

transformations, producing minor structural changes and contributing to a decrease in the biological activity (Bertrand et al., 2015; Sviridov et al., 2015). Moreover, as observed in the study by Dilly and Nannipieri (2001), the response of some specific enzymes activities are correlated with ATP content, which can also provide valuable information on transformation of pesticides. However, it should be remembered that such a study ought to performed immediately after sampling, so that the ATP content may reflect a current microbial activity and changes that occur in microbial biomass.

Hydrolases are another class of enzymes participating in effective pesticides degradation in soil. This group of enzymes functions without redox cofactors. They contribute to breaking bonds in carbon-halogen, amide or ester. The transformation of organophosphorus insecticides is caused by phosphotriesterases, for example, parathion is converted into paraoxon by hydrolysis of the P—S bond or by hydrolysis the O—P bond into diethylthiophosphoric acid and paranitrophenol (Bertrand et al., 2015). Moreover, in soil, chlorohydrolases and amids contribute to the degradation of chlorinated triazines. Chlorohydrolases are responsible for the formation of hydroxyatrazine – an intermediate product, by which amidohydrolases are transformed into cyanuric acid that is readily degraded and mineralized (Elias et al., 2008), as shown in Fig. 2.

The fungicides used in the growing season on plants also reach into soil where they affect the enzymatic activity. The studies by Baćmaga et al. (2015) showed that azoxystrobin inhibits the enzymatic activity of soil. Significant inhibitory changes in enzymatic activity were observed for urease, catalase, acidic and alkaline phosphatase, but no reducing effect on dehydrogenases was detected. Moreover, fungi and bacteria in soil are involved in producing peroxidases, oxygenases and hydrolytic enzymes. They are important for the biodegradation of pesticides and their derivative products. According to Rangasamy et al. (2018), peroxidases produced by soil microorganisms convert 3,4-dichloroaniline into 4,4-tetrachloroazobenzene. However, an important role is also played by auxiliary enzymes, including glucose oxidase and catalase. Those enzymes supply and regulate the concentration of H_2O_2 as peroxidases co-substrate in the environment of the reaction (Tian et al., 2016). As observed by Yun et al. (2006), after a single dose of chlorothalonil, soil microorganisms gradually adapted to the presence of the pesticide and they were capable of degrading it. This fact is confirmed by an increase in the enzymatic activity. However, after the second application of chlorothalonil, one observes an inhibition in the enzymatic activity in acidic and alkaline phosphatase, urease and catalase (Yun et al., 2006), which has an impact on the longer persistence of this substance in the environment.

The health of soil is also determined by the spatial distribution of microorganisms responsible for excreting a variety of enzymes (Nannipieri et al., 2002). According to Blackwood et al. (2006), the majority of microorganisms was located in the rhizosphere zone and in soil particles rich in organic matter. Analysing interactions between roots, soil, microorganisms and anthropogenic compounds is crucial for quantifying rates of enzyme activities (Schimel and Bennett, 2004). It is important for their determination by means of tests providing potential rather than actual information on the enzymatic activity. It is still difficult to unmistakably state in the in situ studies what number of enzymes is being dealt with, because their quantity and activity change spatially. It should also be pointed out that the activity of an enzyme is not always controlled by the respective protein in active cells. Moreover, enzymes in soil can be present in the absence of proliferating and non-proliferating microorganisms (Gianfreda and Ruggiero, 2006). Therefore, scientists still have a problem interpreting the results of enzymatic activities in soil, for example, they find it difficult to distinguish the activity of extracellular enzymes from that of the intracellular ones. Besides, taking a sample and then testing it is far from easy, which is related to the fact that there are few methods available for such research (Šnajdr et al., 2008). It is an area that is constantly developing and improving, which is conditioned by the problems related to the estimation of the impact of various anthropogenic compounds on microbiological activity of soil. Currently various methods are used, including both the simple ones for determining enzymatic activity and the most advanced molecular techniques (Fig. 3).

Göttlein and Stanjek (1996) showed that geostatistical approaches make it possible to detect variations in chemical and biological soil properties at mm to cm scales that vary independently of soil horizons. Therefore, researchers adopt approaches that allow the spatial distribution of enzyme activities to be visualized and/or to be associated with the presence of specific microorganisms depending on the

occurrence of anthropogenic compounds in soil (Marschner et al., 2005; Buée et al., 2007; Dong et al., 2007).

3. Prevention of negative effects of pesticides on biological soil activity

Due to negative effects of introducing pesticides into environment, it is necessary to search for methods that support soil biological activity and at the same time ensure safe and proper degradation of pesticides. This issue is difficult to develop due to a small amount of data on the use of pesticides with other treatments increasing their biodegradation and their impact on microbial activity in soil.

Among issues related to the increase of pesticides degradation, attention should be paid to bioremediation techniques in which microorganisms are introduced as vaccines to degrade toxic compounds. As a result, inoculated bacterial communities enrich the natural environment where they have a chance to adapt, disturbing the microflora of soil. To increase the ability of microorganisms to degrade contaminants, genetic modifications are also introduced. Gong et al. (2016) presented a study in which the genes of hydrolase carbofuran/chlorpyrifos and *gfp* were integrated into biosafety strain *Pseudomonas putida* KT2440. The recombinant strain showed the ability to degrade carbofuran and chlorpyrifos. It also had the potential to be used for in situ soil bioremediation. In the next study, Gong et al. (2018) discussed the recombinant strain *P. putida* KTUe used for degradation of three types of pesticides (organophosphates, pyrethroids, and carbamates). In this work, pesticide-degrading genes, *vgb* and *gfp,* were inserted into chromosomes. The laboratory studies showed that *P. putida* KTUe had the capability of degrading methyl parathion, chlorpyrifos, fenpropathrin, cypermethrin, carbofuran and carbaryl within 30 days when incubated in M9 minimal medium, whereas in research conducted in soil, the pesticides were removed within 15 days. The risk related to the introduction of genetically modified microorganisms into soil involves the transfer of antibiotic resistance genes from recombinants to the indigenous microorganisms and their diffusion in the environment (Zuo et al., 2015).

The studies indicate that biochar is a future-proof material for the remediation of soils contaminated with pesticides. It is produced from the combustion of agricultural biowastes (wood, crop residues, animal residues) by oxygen pyrolysis. This carbon-rich byproduct is used to improve properties (pH, Cation Exchange Capacity – CEC, water holding capacity, fertility) of soil which is degraded and contaminated with inorganic and organic pollutants (Khorram et al., 2016). Furthermore, Ahmad et al. (2014) reported that biochar has the capability of decreasing pesticide bioavailability in the environment. Nevertheless, according to Denyes et al. (2016), biochar has a selective ability to absorb pesticides. In this study, the application of biochar to soil had no effects on adsorption of DDT. In addition, biochar has a positive effect on microbial biomass and activity in soil. The byproduct may provide specific environmental conditions for microorganisms, which can inhabit biochar pores and use carbon as well as other nutrients (Zhu et al., 2017).

Another example of the reduction of the potential environmental hazard due to the use of pesticides is the modification of their physicochemical properties and a proper preparation of their ionic liquids. Novel pesticides are generally characterized by low volatility, solubility, surface tension, high lipophilicity and a moderate octanol-water partition coefficient (Wang et al., 2019; Niu et al., 2018). Several studies describe the use of nanocomposites to control a pesticide release. This is achieved by combining these agrochemicals (pesticides) with polymers, which allows for releasing the required amount of substance at a controlled rate over a specified period of time. There are two ways of combining a polymer with pesticides, i.e. physical and chemical. In the former case, one uses heterogeneous dispersion or encapsulation, while in the latter, the polymer acts as a carrier of the agent. A controlled release of toxic substances to the environment causes less damage to the microorganism community (Puoci et al., 2008). Moreover, the majority of the polymers used for this purpose is biodegradable (polysaccharides and proteins). Therefore, they can be an additional source of nutrients for microorganisms (Roy et al., 2014).

4. Summary

Due to the fact that in modern agriculture, intensive use of pesticides is a common practice all over the world, soil pollution with pesticides may increase (Yang et al., 2006). A significant concentration of active substances of pesticides frequently remains in soil, undergoing biological and physicochemical transformations, influencing microbial growth and enzymatic activity in soils.

In the natural environment, microbial degradation of pesticides consists in the distribution of mixtures of many substances, whereas laboratory tests tend to analyze the distribution of a single active substance. Such tests allow for determining the degradation pathways of individual active substances of pesticides. However, there are hardly any studies which discuss the distribution of mixtures of active substances accumulating in soil under the influence of other physical and chemical soil factors. The use of the methods of genetic engineering and various biotechnological techniques makes it possible to analyze how pesticides are biodegraded by microorganisms. New strains generated by genetic engineering have the ability to degrade more efficiently complex mixtures of various compounds, especially environmental pollutants like pesticides.

Another problem is related to the choice of the method of measuring biological activity: many methods exist and they vary greatly. In some case, it is difficult to select appropriate tests for specific microbiological activities. This state of affairs is conditioned by the lack of standard analysis methods accepted by all laboratories, which are necessary to interpret the results. Moreover, there are differences in sample collecting, storage, pre-treatment and protocols for determining enzymatic and microbiological activities (Gil-Sotres et al., 2005). All these factors influence the comparison of enzyme-encoding genes and the respective enzyme activity in soil. The topic is still very important, because these studies can give insights into the origin of enzymes in soil, determining the influence of various pollutants on soil health.

Acknowledgment

This work was financially supported by Ministry of Science and Higher Education, Poland, under the research project number WZ/WBiIŚ/3/2019

References

Abbas, Z., Akmal, M., Khan, K.S., Hassan, F.U., 2014. Effect of buctril super (bromoxynil) herbicide on soil microbial biomass and bacterial population. Braz. Arch. Biol. Technol. 57, 9–14.

Ahemad, M., Khan, M.S., 2011. Ecotoxicological assessment of pesticides towards the plant growth promoting activities of Lentil (Lens esculentus)-specific *Rhizobium* sp. strain MRL3. Ecotoxicology 20, 661–669.

Ahmad, M., Rajapaksha, A.U., Lim, J.E., Zhang, M., Bolan, N., Mohan, D., Vithanage, M., Lee, S.S., Ok, Y.S., 2014. Biochar as a sorbent for contaminant management in soil and water: a review. Chemosphere 99, 19–33.

Al-Arfaj, A., Abdel-Megeed, A., Ali, H.M., Al-Shahrani, O., 2013. Phyto-microbial degradation of glyphosate in Riyadh area. J. Pure Appl. Microbiol. 7 (2), 1351–1365.

Anastassiades, M., Lehotay, S.J., Stajnbaher, D., Schenck, F.J., 2003. Fast and easy multiresidue method employing acetonitrile extraction/partitioning and “dispersive solid-phase extraction” for the determination of pesticide residues in produce. J. AOAC Internet 86, 412–431.

Arabet, D., Tempel, S., Fons, M., 2014. Effects of a sulfonylurea herbicide on the soil bacterial community. Environ. Sci. Pollut. Res. 21 (8), 5619–5627.

Baćmaga, M., Borowik, A., Kucharski, J., Tomkiel, M., Wyszkowska, J., 2015. Microbial and enzymatic activity of soil contaminated with a mixture of diflufenican + mesosulfuron-methyl + iodosulfuron-methyl-sodium. Environ. Sci. Pollut. Res. 22, 643–656.

Barraclough, D., Kearney, T., Croxford, A., 2005. Bound residues: environmental solution or future problem? Environ. Pollut. 133, 85–90.

Bending, G.D., Rodrıguez-Cruz, M.S., 2007. Microbial aspects of the interaction between

soil depth and biodegradation of the herbicide isoproturon. Chemosphere 66, 664–671.
Bertrand, J.C., Doumenq, P., Guyoneaud, R., Marrot, B., Martin-Laurent, F., Matheron, R., Moulin, P., Soulas, G., 2015. Applied microbial ecology and bioremediation. In: Bertrand, J.C., Caumette, P., Lebaron, P., Matheron, R., Normand, P., Sime-Ngando, T. (Eds.), Environmental Microbiology: Fundamentals and Applications. Springer, Dordrecht.
Bhatt, P., Sharma, A., Gangola, S., Khati, P., Kumar, G., Srivastava, A., 2016. Novel pathway of cypermethrin biodegradation in a *Bacillus* sp. Strain SG2 isolated from cypermethrin-contaminated agriculture field. 3 Biotech 6, 45.
Blackwood, C.B., Dell, C.J., Smucker, A.J.M., Paul, E.A., 2006. Eubacterial communities in different soil macroaggregate environments and cropping systems. Soil Biol. Biochem. 38, 720–728.
Boldt, T.S., Jacobsen, C.S., 1998. Different toxic effects of the sulphonylurea herbicides metsulfuron methyl, chlorsulfuron and thifensulfuron methyl on fluorescent pseudomonads isolated from an agricultural soil. FEMS Microbiol. Lett. 161, 29–35.
Bolshakov, D.S., Amelin, V.G., Tretyakov, A.V., 2014. Determination of polar pesticides in soil by micellar electrokinetic chromatography using QuEChERS sample preparation. J. Anal. Chem. 69, 89–97.
Buée, M., Courty, P.E., Mignot, D., Garbaye, J., 2007. Soil niche effect on species diversity and catabolic activities in an ectomycorrhizal fungal community. Soil Biol. Biochem. 39, 1947–1955.
Cai, X.Y., Sheng, G.Y., Liu, W.P., 2007. Degradation and detoxification of acetochlor in soils treated by organic and thiosulfate amendments. Chemosphere 66, 286–292.
Chen, K., Huang, L.L., Xu, C.F., Liu, X.M., He, J., Zinder, S.H., Li, S.P., Jiang, J.D., 2013. Molecular characterization of the enzymes involved in the degradation of a brominated aromatic herbicide. Mol. Microbiol. 89 (6), 1121–1139.
Chen, S.H., Yang, L., Hu, M.Y., Liu, J.J., 2011. Biodegradation of fenvalerate and 3-phenoxybenzoic acid by a novel *Stenotrophomonas* sp. strain ZS-S-01 and its use in bioremediation of contaminated soils. Appl. Microbiol. Biotechnol. 90, 755–767.
Chen, S.K., Edwards, C.A., Subler, S., 2001. Effect of fungicides benomyl, captan and chlorothalonil on soil microbial activity and nitrogen dynamics in laboratory incubations. Soil Biol. Biochem. 33, 1971–1980.
Chowdhury, A., Pradhan, S., Saha, M., Sanyal, N., 2008. Impact of pesticides on soil microbiological parameters and possible bioremediation strategies. Indian J. Microbiol. 48 (1), 114–127. https://doi.org/10.1007/s12088-008-0011-8.
Crespo-Corral, E., Santos-Delgado, M.J., Polo-Diez, L.M., Soria, A.C., 2008. Determination of carbamate, phenylurea and phenoxy acid herbicide residues by gas chromatography after potassium tert-butoxide/dimethyl sulphoxide/ethyl iodide derivatization reaction. J. Chromatogr. A 1209, 22–28.
Cycoń, M., Piotrowska-Seget, Z., 2016. Pyrethroid-degrading microorganisms and their potential for the bioremediation of contaminated soils. Rev. Front. Microbiol. 7, 1–26.
Cycoń, M., Piotrowska-Seget, Z., Kozdrój, J., 2010. Dehydrogenase activity as an indicator of different microbial responses to pesticide-treated soils. Chem. Ecol. 26, 243–250.
Das, A.C., Das, S.J., Dey, S., 2012. Effect of herbicides on microbial biomass in relation to availability of plant nutrients in soil. J. Crop Weed 8 (1), 129–132.
Das, A.C., Mukherjee, D., 2000. Soil application of insecticides influences micro-organisms and plant nutrients. Appl. Soil Ecol. 14, 55–62.
Das, S.K., Varma, A., 2011. Role of enzymes in maintaining soil health. In: Shukla, G., Varma, A. (Eds.), Soil Enzymology, Soil Biology 22. Springer-Verlag, Berlin Heidelberg.
Datta, R., Anand, S., Moulick, A., Baraniya, D., Pathan, S.I., Rejsek, K., Vranová, V., Sharma, M., Sharma, D., Kelkar, A., Formánek, P., 2017. How enzymes are adsorbed on soil solid phase and factors limiting its activity: a Review. Int. Agrophys. 31, 287–302.
Denyes, M.J., Rutter, A., Zeeb, B.A., 2016. Bioavailability assessments following biochar and activated carbon amendment in DDT-contaminated soil. Chemosphere 144, 1428–1434.
Dilly, O., Nannipieri, P., 2001. Response of ATP content, respiration rate and enzyme activities in an arable and a forest soil to nutrient additions. Biol. Fertil. Soils 34, 64–72.
Dong, S., Brooks, D., Jones, M.D., Grayston, S.J., 2007. A method for linking in situ activities of hydrolytic enzymes to associated organisms in forest soils. Soil Biol. Biochem. 39, 2414–2419.
Eizuka, T., Ito, A., Chida, T., 2003. Degradation of ipconazole by microorganisms isolated from paddy soil. J. Pestic. Sci. 28, 200–207.
Elias, M., Dupuy, J., Merone, L., Mandrich, L., Porzio, E., Moniot, S., Rochu, D., Lecomte, C., Rossi, M., Masson, P., Manco, G., Chabriere, E., 2008. Structural basis for natural lactonase and promiscuous phosphotriesterase activities. J. Mol. Biol. 379, 1017–1028.
El-Nahhal, Y., El-Hams, S., 2017. Effects of Bromacil, malathion and thiabendazole on Cyanobacteria mat growth. Int. J. Appl. Sci. Res. Rev. 4, 1. https://doi.org/10.21767/2349-7238.100053.
Erick, R.B., Juan, A.O., Paulino, P., Torres, L.G., 2006. Removal of aldrin, dieldrin, heptachlor, and heptachlor epoxide using activated carbon and/or pseudomonas fluorescens free cell cultures. J. Environ. Sci. Health B 41, 553–569.
Feng, Z., Li, Q., Zhang, J., Zhang, J., Huang, X., Lu, P., Li, S., 2012. Microbial degradation of fomesafen by a newly isolated strain *Pseudomonas zeshuii* BY-1 and the biochemical degradation pathway. J. Agric. Food Chem. 60 (29), 7104–7110.
Fenlon, K.A., Jones, K.C., Semple, K.T., 2007. Development of microbial degradation of cypermethrin and diazinon in organically and conventionally managed soils. J. Environ. Monit. 9, 510–515.
Fragoeiro, S., Magan, N., 2008. Impact of *Trametes versicolor* and *Phanerochaete chrysosporium* on differential breakdown of pesticide mixtures in soil microcosms at two water potentials and associated respiration and enzyme activity. Int. Biodeter. Biodegr. 62, 376–383.
Gianfreda, L., Rao, M., 2008. Interactions between xenobiotics and microbial and enzymatic soil activity. Environ. Sci. Technol. 38, 269–310.
Gianfreda, L., Rao, M.A., 2010. The influence of pesticides on soil enzymes. In: Shukla, G., Varma, A. (Eds.), Soil Enzymology. Soil Biology Series No. 22. Springer Verlag, Berlin/Heidelberg, Germany, pp. 293–312.
Gianfreda, L., Ruggiero, P., 2006. Enzyme activities in soil. In: Nannipieri, P., Smalla, K. (Eds.), Nucleic Acids and Proteins in Soil. Springer-Verlag, Berlin Heidelberg, pp. 257–297.
Gil-Sotres, F., Trasar-Cepeda, C., LeirÃs, M.C., Seoane, S., 2005. Different approaches to evaluating soil quality using biochemical properties. Soil Biol. Biochem. 37, 877.
Gong, T., Liu, R., Che, Y., Xu, X., Zhao, F., Yu, H., Song, C., Liu, Y., Yang, C., 2016. Engineering *Pseudomonas putida* KT2440 for simultaneous degradation of carbofuran and chlorpyrifos. Microb. Biotechnol. 9, 792–800.
Gong, T., Xu, X., Dang, Y., Kong, A., Wu, Y., Liang, P., Wang, S., Yu, H., Xu, P., Yang, C., 2018. An engineered *Pseudomonas putida* can simultaneously degrade organophosphates, pyrethroids and carbamates. Sci. Total Environ. 628–629, 1258–1265.
Gonzalez-Lopez, J., Martinez-Toledo, M.V., Salermon, V., Rodelas, B., 1993. Studies on the effects of the insecticide phorate and malathion on soil microorganisms. Environ. Toxicol. Chem. 12, 1209–1214.
Göttlein, A., Stanjek, H., 1996. Micro-scale variation of solid-phase properties and soil solution chemistry in a forest podzol and its relation to soil horizons. Eur. J. Soil Sci. 47, 627–636.
Gundi, V., Viswanath, B., Chandra, M.S., Kumar, V.N., Reddy, B.R., 2007. Activities of cellulase and amylase in soils as influenced byinsecticide interactions. Ecotox. Environ. Safe 68, 278–285.
He, Y.H., Shen, D.S., Fang, C.R., He, R., Zhu, Y.M., 2006. Effect of metsulfuron-methyl on the microbial population and enzyme activities in wheat rhizosphere soil. J. Environ. Sci. Health B 41, 269–284.
Hsiao, Y.L., Ho, W.H., Yen, J.H., 2013. Vertical distribution in soil column and dissipation in soil of benzoylurea insecticides diflubenzuron, flufenoxuron and novaluron and effect on the bacterial community. Chemosphere 90 (2), 380–386.
Hu, G.P., Zhao, Y., Song, F.Q., Liu, B., Vasseur, L., Douglas, C., You, M.S., 2014. Isolation, identification and cyfluthrin-degrading potential of a novel *Lysinibacillus sphaericus* strain, FLQ-11-1. Res. Microbiol. 165, 110–118.
Huang, X., He, J., Sun, X.F., Sun, J.Q., Li, Y.F., Shen, J.J., Li, S.P., 2010. Characterization and molecular mechanism of a naturally occurring metsulfuron-methyl resistant strain of Pseudomonas aeruginosa. World J. Microbiol. Biotechnol. 26 (3), 515–521.
Hussain, S., Siddique, T., Saleem, M., Arshad, M., Khalid, A., 2009. Impact of pesticides on soil microbial diversity, enzymes, and biochemical reactions. Adv. Agron. 102, 159–200.
Jarvis, N.J., 2007. Review of non-equilibrium water flow and solute transport in soil macropores: principles, controlling factors and consequences for water quality. Eur. J. Soil Sci. 58, 523–546.
Jian, S., Li, J., Chen, J., Wang, G., Mayes, M.A., Dzantor, K.E., Hui, D., Luo, Y., 2016. Soil extracellular enzyme activities, soil carbon and nitrogen storage under nitrogen fertilization: a meta-analysis. Soil Biol. Biochem. 101, 32–43.
Kaczyński, P., 2017. Large-scale multi-class herbicides analysis in oilseeds by rapid one-step QuEChERS-based extraction and cleanup method using liquid chromatography–tandem mass spectrometry. Food Chem. 230, 411–422.
Kaczyński, P., Łozowicka, B., Jankowska, M., Hynko, I., 2016. Rapid determination of acid herbicides in soil by liquid chromatography with tandem mass spectrometric detection based on dispersive solid phase extraction. Talanta 152, 127–136.
Kalam, A., Mukherjee, A.K., 2001. Influence of hexaconazole, carbofuran and ethionon soil microflora and dehydrogenase activities in soil and intact cell. Indian J. Exp. Biol. 39, 90–94.
Khan, M.S., Zaidi, A., Rizvi, P.Q., 2006. Biotoxic effects of herbicides on growth, nodulation, nitrogenase activity, and seed production in chickpeas. Commun. Soil Sci. Plant Anal. 37, 1783–1793.
Khorram, M., Zhang, Q., Lin, D., Zheng, Y., Fang, H., Yu, Y., 2016. Biochar: a review of its impact on pesticide behavior in soil environments and its potential applications. J. Environ. Sci. 44, 269–279.
Kim, I.S., Ryu, J.Y., Hur, G.H., 2004. *Sphingomonas* sp. Strain SB5 degrades carbofuran to a new metabolite by hydrolysis at the furanyl ring. J. Agric. Food Chem. 52, 2309–2314.
Kumar, S., Chaudhuri, S., Maiti, S.K., 2014. Soil dehydrogenase enzyme activity in natural and mine soil - a review. Middle-East J. Sci. Res. 13 (7), 898–906.
León-Santiesteban, H.H., Rodríguez-Vázquez, R., 2017. Fungal degradation of organochlorine pesticides. In: Singh, S.N. (Ed.), Microbe-Induced Degradation of Pesticides. Springer, pp. 131–149.
Li, Y., Chen, Q., Wang, C.H., Cai, S., He, J., Huang, X., Li, S.P., 2013. Degradation of acetochlor by consortium of two bacterial strains and cloning of a novel amidase gene involved in acetochlor-degrading pathway. Bioresour. Technol. 148, 628–631.
Lin, C.H., Lerch, R.N., Kremer, R.J., Garrett, H.E., 2011. Stimulated rhizodegradation of atrazine by selected plant species. J. Environ. Qual. 40, 1113–1121.
Liu, J., Huang, W., Han, H., She, C., Zhong, G., 2015. Characterization of cell-free extracts from fenpropathrin-degrading strain *Bacillus cereus* ZH-3 and its potential for bioremediation of pyrethroid-contaminated soils. Sci. Total Environ. 523, 50–58.
Łozowicka, B., Kaczyński, P., Wolejko, E., Piekutin, J., Sagitov, A., Toleubayev, K., Isenova, G., Abzeitova, E., 2016. Evaluation of organochlorine pesticide residues in soil and plants from East Europe and Central Asia. Desalin. Water Treat. 57 (3), 1310–1321.
Łozowicka, B., Mojsak, P., Kaczyński, P., Konecki, R., Borusiewicz, A., 2017. The fate of spirotetramat and dissipation metabolites in Apiaceae and Brassicaceae leaf-root and soil system under greenhouse conditions estimated by modified QuEChERS/LC-MS/

MS. Sci. Total Environ. 15 (603-604), 178–184.
Mahdi, J.E., Abbott, L.K., Pauli, N., Solaiman, Z.M., 2017. Biological indicators for soil health: potential for development and use of on-Farm tests. In: Varma, A., Sharma, A. (Eds.), Modern Tools and Techniques to Understand Microbes. Springer, pp. 123–134.
Mantzos, N., Karakitsou, A., Zioris, I., Leneti, E., Konstantinou, I., 2013. QuEChERS and solid phase extraction methods for the determination of energy crop pesticides in soil, plant and runoff water matrices. Int. J. Environ. Anal. Chem. 93, 1566–1584.
Marschner, P., Grierson, P.F., Rengel, Z., 2005. Microbial community composition and functioning in the rhizosphere of three Banksia species in native woodland in Western Australia. Appl. Soil Ecol. 28, 191–201.
Megadi, V.B., Tallur, P.N., Mulla, S.I., Ninnekar, H.Z., 2010. Bacterial degradation of fungicide captan. J. Agric. Food Chem. 58 (24), 12863–12868.
Mele, P.M., Crowley, D.E., 2008. Application of self-organizing maps for assessing soil biological quality. Agric., Ecosyst. Environ. 126, 139–152.
Mercadier, C., Vega, D., Bastide, J., 1997. Iprodione degradation by isolated soil microorganisms. FEMS Microbiol. Ecol. 23, 207–215.
Miyamoto, T., Ishii, H., Seko, T., Kobori, S., Tomita, Y., 2009. Occurrence of Corynespora cassiicola isolates resistant to boscalid on cucumber in Ibaraki Prefecture. Japan Plant Pathol. 58 (6), 1144–1151.
Mohamed, M.S., 2009. Degradation of methomyl by the novel bacterial strain *Stenotrophomonas maltophilia* M1. Electron. J. Biotechnol. 12 (4), 1–6.
Mommaerts, V., Sterk, G., Smagghe, G., 2006. Hazards and uptake of chitin synthesis inhibitors in bumblebees Bombus terrestris. Pest Manag. Sci. 62, 752–758.
Monkiedje, A., Spiteller, M., 2005. Degradation of metalaxyl and mefenoxam and effects on the microbiological properties of tropical and temperate soils. Int. J. Environ. Res. Public Health 2 (2), 272–285.
Muñoz-Leoz, B., Ruiz-Romera, E., Antigüedad, I., Garbisu, C., 2011. Tebuconazole application decreases soil microbial biomass and activity. Soil Biol. Biochem. 43, 2176–2183.
Myresiotis, C.K., Vryzas, Z., Papadopoulou-Mourkidou, E., 2012. Biodegradation of soil-applied pesticides by selected strains of plant growth-promoting rhizobacteria (PGPR) and their effects on bacterial growth. Biodegradation 23, 297–310.
Nannipieri, P., Giagnoni, L., Renella, G., Puglisi, E., Ceccanti, B., Masciandaro, G., Fornasier, F., Moscatelli, M.C., Marinari, S., 2012. Soil enzymology: classical and molecular approaches. Biol. Fertil. Soils 48, 743–762.
Nannipieri, P.B., Kandler, E., Ruggiero, P., 2002. Enzyme activity and microbial and biochemical processes in soil. In: Dick, R.P., Burns, R.G. (Eds.), Enzymes in the Environment: Activity, Ecology and Applications. Marcel Dekker, New York, USA, pp. 1–33.
Ndiaye, E.L., Sandeno, J.M., McGrath, D., Dick, R.P., 2000. Integrative biological indicators for detecting change in soil quality. Am. J. Altern. Agric. 15, 26–36.
Nie, Z.J., Hang, B.J., Cai, S., Xie, X.T., He, J., Li, S.P., 2011. Degradation of cyhalofop-butyl (Cyb) by *Pseudomonas* azotoformans strain qdz-1 and cloning of a novel gene encoding cyb-hydrolyzing esterase. J. Agric. Food Chem. 59 (11), 6040–6046.
Niewiadomska, A., 2004. Effect of carbendazim, imazetapir and thiram on nitrogenase activity,the number of microorganisms in soil and yield of red clover (*Trifolium pretense* L). Pol. J. Environ. Stud. 13, 403–410.
Niu, J., Zhang, Z., Tang, J., Tang, G., Yang, J., Wang, W., Huo, H., Jiang, N., Li, J., Cao, Y., 2018. Dicationic ionic liquids of herbicide 2,4-D with reduced negative effects on environment. J. Agric. Food Chem. 66 (40), 10362–10368.
Oberemok, V.V., Laikova, K.V., Gninenko, Y.I., Zaitsev, A.S., Nyadar, P.M., Adeyemi, T.A., 2015. A short history of insecticides. J. Plant Prot. Res. 55 (3), 221–226.
Paingankar, M., Jain, M., Deobagkar, D., 2005. Biodegradation of allethrin, a pyrethroid insecticide, by an Acidomonas sp. Biotechnol. Lett. 27, 1909–1913.
Pal, R., Das, P., Chakrabarti, K., Chakraborty, A., Chowdhury, A., 2008. Side effects of pencycuron on nontarget soil microorganisms in waterlogged soil: field experiment. Appl. Soil Ecol. 38, 161–167.
Panda, J., Kanjilal, T., Das, S., 2018. Optimized biodegradation of carcinogenic fungicide Carbendazim by *Bacillus licheniformis* JTC-3 from agro-effluent. Biotechnol. Res. Innov. 2 (1), 45–57.
Patnaik, G.K., Kanungo, P.K., Adhya, T.K., Rao, V.R., 1996. Effect of repeatedapplications of gamma-hexachlorocyclohexane (gamma-HCH) on nitrogenase activityand nitrogen-fixing bacteria associated with rhizosphere of tropical rice. Microbiol. Res. 151, 375–378.
Peysson, W., Vulliet, E., 2013. Determination of 136 pharmaceuticals and hormones in sewage sludge using quick, easy, cheap, effective, rugged and safe extraction followed by analysis with liquid chromatography-time-of-flight-mass spectrometry. J. Chromatogr. A 1290, 46–61.
Pinto, C.G., Laespada, M.E.F., Martin, S.H., Ferreira, A.M.C., Pavon, J.L.P., Cordero, B.M., 2010. Simplified QuEChERS approach for the extraction of chlorinated compounds from soil samples. Talanta 81, 385–391.
Pizzul, L., Castillo Mdel, P., Stenstrom, J., 2009. Degradation of glyphosate and other pesticides by ligninolytic enzymes. Biodegradation 20, 751–759.
PPDB, 2019. Pesticide Properties DataBase. (Accessed 1 May 2019). https://sitem.herts.ac.uk/aeru/ppdb/en/atoz.htm.
Puoci, F., Iemma, F., Spizzirri, U.G., Cirillo, G., Curcio, M., Picci, N., 2008. Polymer in agriculture: a review. J. Agric. Biol. Sci. 3 (1), 299–314.
Rangasamy, K., Athiappan, M., Devarajan, N., Samykannu, G., Parray, J.A., Aruljothi, K.N., Shameem, N., Alqarawi, A.A., Hashem, A., Abd Allah, E.F., 2018. Pesticide degrading natural multidrug resistance bacterial flora. Microb. Pathog. 114, 304–310.
Ratcliff, A.W., Busse, M.D., Shestak, C.J., 2006. Changes in microbial community structure following herbicide (glyphosate) additions to forest soils. Appl. Soil Ecol. 34, 114–124.
Riffaldi, R., Levi-Minzi, R., Cardelli, R., Palumbo, S., Saviozzi, A., 2006. Soil biological activities in monitoring the bioremediation of diesel oil-contaminated soil. Water Air Soil Pollut. 170, 3–15.
Romdhane, S., Devers-Lamrani, M., Martin-Laurent, F., Calvayrac, C., Rocaboy-Faquet, E., Riboul, D., Cooper, J.F., Barthelmebs, L., 2016. Isolation and characterization of *Bradyrhizobium* sp. SR1 degrading two β-triketone herbicides. Environ. Sci. Pollut. Res. Int. 23, 4138–4148.
Roy, A., Singh, S.K., Bajpai, J., Bajpai, A.K., 2014. Controlled pesticide release from biodegradable polymers. Cent. Eur. J. Chem. 12, 453–469.
Saikia, N., Gopal, M., 2004. Biodegradation of beta-cyfluthrin by fungi. J. Agric. Food Chem. 52, 1220–1223.
Saikia, N., Das, S.K., Patel, B.K.C., Niwas, R., Singh, A., Gopal, M., 2005. Biodegradation of beta-cyfluthrin by *Pseudomonas stutzeri* strain S1. Biodegradation 16, 581–589.
Santacruz, G., Bandala, E., Torres, L.G., 2005. Chlorinated pesticidas (2,4–D and DDT) biodegradation at high concentrations using immobilized Pseudomonas fluorescens. J. Environ. Sci. Heal. 40 (4), 571–583.
Santos-Delgado, M.J., Crespo-Corral, E., Polo-Diez, L.M., 2000. Determination of herbicides in soil samples by gas chromatography: optimization by the simplex method. Talanta 53, 367–377.
Sarnaik, S.S., Kanekar, P.P., Raut, V.M., Taware, S.P., Chavan, D.S., Bhadbhade, B.J., 2006. Effect of application of different pesticides to soybean on the soil microflora. J. Environ. Biol. 27, 423–426.
Sasikala, C., Jiwal, S., Rout, P., Ramya, M., 2012. Biodegradation of chlorpyrifos by bacterial consortium isolated from agriculture soil. World J. Microbiol. Biotechnol. 28, 1301–1308. https://doi.org/10.1007/s11274-011-0879-z.
Schauer, F., Borriss, R., 2004. Biocatalysis and biotransformation. In: Tkacz, J.S., Lange, L. (Eds.), Advances in Fungal Biotechnology for Industry, Agriculture and Medicine. Springer, Boston, MA, pp. 237–306.
Schimel, J.P., Bennett, J., 2004. Nitrogen mineralization: challenges of a changing paradigm. Ecology 83, 591–602.
Singh, B., Singh, K., 2016. Microbial degradation of herbicides. J. Crit. Rev. Microbiol. 42 (2), 245–261.
Singh, K., 2016. Microbial and enzyme activities of saline and sodic soils. Land Degrad. Dev. 27, 706–718.
Šnajdr, J., Valášková, V., Merhautová, V., Herinková, J., Cajthaml, T., Baldrian, P., 2008. Spatial variability of enzyme activities and microbial biomass in the upper layers of Quercus petraea forest soil. Soil Biol. Biochem. 40, 2068–2075.
Song, H., Zhou, Z., Liu, Y., Deng, S., Xu, H., 2015. Kinetics and mechanism of fenpropathrin biodegradation by a newly isolated Pseudomonas aeruginosa sp. strain JQ-41. Curr. Microbiol. 71, 326–332.
Sørensen, S.R., Bending, G.D., Jacobsen, C.S., Walker, A., Aamand, J., 2003. Microbial degradation of isoproturon and related phenylurea herbicides in and below agricultural fields. FEMS Microb. Ecol. 45 (1), 1–11.
Sun, L., Dong, Y., Zhou, Y., Yang, M., Zhang, C., Rao, Z., Zhang, X.E., 2004. Crystallization and preliminary X-ray studies of methyl parathion hydrolase from Pseudomonas sp. WBC-3. Acta Crystallogr. D Biol. Crystallogr. 60 (5), 954–956.
Sviridov, A.V., Shushkova, T.V., Ermakova, I.T., Ivanova, E.V., Epiktetov, D.O., Leontievsky, A.A., 2015. Microbial degradation of glyphosate herbicides. Prikl. Biokhim. Mikrobiol. 51 (2), 183–190.
Swissa, N., Nitzan, Y., Langzam, Y., Cahan, R., 2014. Atrazine biodegradation by a monoculture of Raoultella planticolaisolated from a herbicides wastewater treatment facility. Int. Biodeter. Biodeg. 92, 6–11.
Tejada, M., Gómez, I., Garcia-Martinez, A.M., Osta, P., Parrado, J., 2011. Effects of prochloraz fungicide on soil enzymatic activities and bacterial communities. Ecotox. Environ. Safe 74, 1708–1714.
Tian, J.H., Pourcher, A.M., Peu, P., 2016. Isolation of bacterial strains able to metabolize lignin and lignin-related compounds. Lett. Appl. Microbiol. 63, 30–37.
Van Eerd, L.L., Hoagland, R.E., Zablotowicz, R.M., Hall, J.C., 2003. Pesticide metabolism in plants and microorganisms. Weed Sci. 51 (4), 472–495.
Verma, J.P., Jaiswal, D.K., Sagar, R., 2014. Pesticide relevance and their microbial degradation: a-state-of-art. Rev. Environ. Sci. Biotechnol. 13, 429–466.
Wang, B., Ma, Y., Zhou, W., Zheng, J., Zhu, J., He, J., Li, S., 2011. Biodegradation of synthetic pyrethroids by Ochrobactrum tritici strain pyd-1. World J. Microbiol. Biotechnol. 27, 2315–2324.
Wang, M.C., Gong, M., Zang, H.B., Hua, X.M., Yao, J., Pang, Y.J., Yang, Y.H., 2006. Effect of methamidophos and urea application on microbial communities in soilsas determined by microbial biomass and community level physiological profiles. J. Environ. Sci. Health B 41, 399–413.
Wang, W., Zhu, J., Tang, G., Huo, H., Zhang, W., Liang, Y., Dong, H., Yang, J., Cao, Y., 2019. Novel herbicide ionic liquids based on nicosulfuron with increased efficacy. New J. Chem. 43, 827–833.
Wang, Y.S., Chen, W.C., Lin, L.C., Yen, J.H., 2010. Dissipation of herbicides chlorsulfuron and imazosulfuron in the soil and the effects on the soil bacterial community. J. Environ. Sci. Health B 45, 449–455.
Webber, M.A., Whitehead, R.N., Mount, M., Loman, N.J., Pallen, M.J., Piddock, L.J.V., 2015. Parallel evolutionary pathways to antibiotic resistance selected by biocide exposure. J. Antimicrob. Chemother. 70, 2241–2248.
White, P.M., Potter, T.L., Culbreath, A.K., 2010. Fungicide dissipation and impact on metolachlor aerobic soil degradation and soil microbial dynamics. Sci. Total Environ. 408, 1393–1402.
Widenfalk, A., Bertilsson, S., Sundh, I., Goedkoop, W., 2008. Effects of pesticides on community composition and activity of sediment microbes – responses at various levels of microbial community organization. Environ. Pollut. 152, 576–584.
Wołejko, E., Kaczyński, P., Łozowicka, B., Wydro, U., Borusiewicz, A., Hrynko, I., Konecki, R., Snarska, K., Dec, D., Malinowski, P., 2017. Dissipation of S-metolachlor in plant and soil and effect on enzymatic activities. Environ. Monit. Assess. 189 (7), 355–370.

World Health Organization & International Programme on Chemical Safety, 2010. The WHO Recommended Classification of Pesticides by Hazard and Guidelines to Classification 2009. World Health Organization, Geneva. http://www.who.int/iris/handle/10665/44271.

Wyszkowska, J., Boros, E., Kucharski, J., 2008. Enzymatic activity of nickel-contaminated soil. J. Elementol. 13 (1), 139–151.

Yang, C., Hamel, C., Vujanovic, V., Gan, Y., 2012. Nontarget effects of foliar fungicide application on the rhizosphere: diversity of nifH gene and nodulation in chickpea field. J. Appl. Microbiol. 112 (5), 966–974.

Yang, Z.X., Liu, S.Q., Zheng, D.W., Feng, S.D., 2006. Effects of cadmium, zinc and lead on soil enzyme activities. J. Environ. Sci. 18, 1135–1141.

Yun, L.Y., Shan, M., Fang, H., Wang, X., Xiao, Q.C., 2006. Responses of soil microorganisms and enzymes to repeated applications of chlorothalonil. J. Agric. Food Chem. 54, 10070–10075.

Zhang, Y., Wang, H., Wang, X., Hu, B., Zhang, C., Jin, W., Zhu, S., Hu, G., Hong, Q., 2017. Identification of the key amino acid sites of the carbendazim hydrolase (MheI) from a novel carbendazim-degrading strain *Mycobacterium* sp. SD-4. J. Hazard. Mater. 331, 55–62.

Zhao, W., Xu, L., Li, D., Li, X., Wang, C., Zheng, M., Pan, C., Qiu, L., 2015. Biodegradation of thifensulfuron-methyl by *Ochrobactrum* sp. in liquid medium and soil. Biotechnol. Lett. 37, 1385–1392.

Zhu, X., Chen, B., Zhu, L., Xinb, B., 2017. Effects and mechanisms of biochar-microbe interactions in soil improvement and pollution remediation: a review. Environ. Pollut. 227, 98–115.

Zuo, Z., Gong, T., Che, Y., Liu, R., Xu, P., Jiang, H., Qiao, C., Song, C., Yang, C., 2015. Engineering *Pseudomonas putida* KT2440 for simultaneous degradation of organophosphates and pyrethroids and its application in bioremediation of soil. Biodegradation 26, 223–233.