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The effect of natural and biological pesticides on the degradation of synthetic pesticides

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Abstract: Chemical plant protection methods have been used for decades. For some time now, society has paid attention to the hazards to human health resulting from the excessive use of chemical protection products. The presence of plant protection agent residues in crops causes changes in the natural environment, including biodiversity loss and the appearance of organisms harmful to plants, resistant to plant protection agents. To protect the health of humans, animals, and the environment, the principles of integrated plant protection have been introduced, giving priority to biological plant protection methods, for example, the use of biological active substances containing microorganisms (bacteria, yeasts, fungi) and natural substances. Microorganisms, as well as other natural substances, can accelerate the degradation of chemical plant protection products present in the environment and agricultural products. This review paper focuses on the effect of natural and biological pesticides on the degradation of synthetic pesticides. The most important and most perspective in integrated pest management (IPM) systems are *Bacillus* spp. and *Trichoderma* spp. because their effectiveness in pesticide degradation and the large number of commercial preparations containing these microorganisms available on the market. The application of biological pesticides recommended in IPM systems could significantly improve the quality of the soil, environment, and human health.

Keywords: pesticide; biocontrol; biodegradation; biopesticides; natural active substances

From January 1, 2014, all professional users of plant protection products (PPP) must apply the principles of the integrated plant protection scheme, according to provisions of Article 14 of Directive 2009/128/EC and of Regulation (EC) No. 1107/2009. The use of chemical plant protection products (PPP) is limited to a necessary minimum, to prevent economic losses in the yield [Council Directive 2009; Comission Regulation (EC) No. 1107/2009].

The integrated pest management scheme means the careful consideration of all available pest control techniques and the integration of measures that discourage the development of pest populations and keep pesticides to acceptable levels (Matyjaszczyk 2015).

Integrated plant protection is a method for protecting plants against harmful organisms, giving priority to the use of non-chemical methods: biological, physical and other non-chemical methods ensuring protection against pests. At the same time, it uses the accumulated knowledge on biology and the harmful effects of those organisms, as well as on antagonistic microorganisms, to safely remove pests from the environment (Korniłowicz-Kowalska 2000; Jensen 2016; Ministry of Agriculture and Rural Development 2022). Non-chemical plant protection methods include crop rotation, reasonable levels of fertilising, liming, drainage, irrigation, and the use of resistant or highly tolerant varieties (Gacek 2016).

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Biological plant protection is a method for pest control, and for the prevention of and fighting crop diseases using natural agents and beneficial organisms. Microorganisms that are agrophage competitors or pathogens are used, such as bacteria, fungi, protozoa, beneficial microorganisms (mites and predatory insects), viruses (used as ingredients of insecticide formulations), natural substances of plant (extracts) and animal origin, as well as semiochemicals (Wolny 2003; Kempka 2014).

By using biopesticides for plant protection, the development of pest resistance to chemical PPPs is prevented, and pesticide residue in the food and environment are maintained at a minimum level, improving the safety of humans and animals (Dominik & Schonthaler 2012).

Biopesticides account for about 5% of the total crop protection market. The number of biopesticides registered in the European Union (EU) is lower than that in countries, like China, India, or the United States, which results from the complex registration processes (Damalas & Koutroubas 2018).

This review paper focuses on the effect of natural and biological pesticides on the degradation of synthetic pesticides.

Table 1 presents a review of microorganisms and natural active substances approved in the European Union (as of February 2022), allocated to the relevant groups: bacteria, fungi, yeast, viruses, inorganic compounds, and other. The mechanisms of action used by the biocontrol agents, microorganisms and active substances to protect plants against pests, are also described.

Biodegradation of pesticides. Biodegradation is a process by which a pesticide is transformed into benign substances that are environmentally compatible. The degradation of pesticides can occur in plants, in the soil, and in water. Microorganisms degrading pesticides may be naturally present and/or intentionally introduced into the environment. The most common type of degradation is carried out in the soil by microorganisms, especially fungi, bacteria and yeasts, which use pesticides as a food and a source of energy. Organisms with the highest pesticide degradation activity are bacteria belonging to the *Arthrobacter, Bacillus, Corynebacterium, Flavobacterium*, *Pseudomonas* and *Rhodococcus* genera, fungi from the *Penicillium, Aspergillus, Fusarium* and *Trichoderma* genera, and the yeast species *Saccharomyces cerevisiae* (Różański 1992; Wróblewska-Krepsztul et al. 2017).

The microbiological degradation of pesticides can occur as a result of:

- enzymatic reactions – microorganisms use pesticides as a source of carbon, nitrogen and energy (fast decomposition), or these reactions are random transformations using extracellular enzymes (slow decomposition). The degradation occurs, for example, during oxidation, reduction, and hydrolysis reactions, transforming organic chemical compounds into small non-toxic molecules, i.e., carbon dioxide, nitrates, phosphates, ammonia, and water (Maloney 2001; Prabha et al. 2017; Huang et al. 2018);
- non-enzymatic reactions – changes in the environmental pH by microorganism metabolites or through the production of compounds interacting with pesticides (Różański 1992; Frąc 2019);
- cometabolism – independent cooperation of organisms in the form of substrate modification through oxidation and/or reduction, without using the product as a source of carbon and energy by that organism. The resultant product becomes available to another organism, which benefits from its decomposition. Following a change in the structure of molecules, a potentially toxic substance is removed from the environment or its toxicity is reduced. One of formulations metabolised this way is dichlorodiphenyltrichloroethane (DDT) (You et al. 1996; Baczyński et al. 2008).

The microbiological degradation of pesticides is influenced by factors including the number and type of microorganisms, metabolic activity of a given microorganism, microorganism resistance to environmental conditions, concentration and chemical structure of the processed pesticide, and environmental factors, like the pH, temperature, humidity, light, salinity, nutrients availability, and oxygen and carbon dioxide levels (Aislabie & Lloyd-Jones 1995; Huang et al. 2018). Table 2 presents a review of the literature on synthetic pesticide degradation by microorganisms and natural active substances used for plant protection, allocated to the relevant group: bacteria, fungi, yeast and inorganic compounds.

OVERVIEW OF PUBLISHED RESULTS

Microorganisms present in biopesticides are responsible for the degradation of the synthetic pesticide residue found in the environment. The literature

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Table 1. A review of natural and biological active substances used in plant protection used in the European Union*

Type	Active substance	Agent type	Mode of action**
Bacteria	*Bacillus amyloliquefaciens*	fungicide	antibiosis, effects of lytic enzymes, effective colonization of plant surfaces, competing for nutrients and induction of natural resistance mechanisms in plants
	Bacillus firmus	nematicide	production of enzymes and phytohormone, degradation of root exudates
	Bacillus pumilus	fungicide	preventing the germination of fungal spores on plants by forming a physical barrier between the spores and the leaf surface
	Bacillus subtilis	fungicide	production of substances disrupting functions of fungal cell membrane, competing for living space and nutrients, and induction of natural defence mechanisms in plants
	Bacillus thuringiensis	insecticide	gastric effect on larvae – in contact with digestive juices of a host it releases D-endotoxin that paralyses muscles of the digestive system, stopping larval trophic activity
	Pasteuria nishizawae	nematicide, insecticide	penetration of nematode epidermis, leads to the pest death
	Pseudomonas spp.	fungicide	induction of the resistance – production of siderophores leading to a restriction in plant root pathogen growth
	Spinosad – a chemical compound found in *Saccharopolyspora spinosa*	insecticide	stimulation of the insect's nervous system leading to involuntary muscle contractions and paralysis in the pest
	Streptomyces spp.	fungicide, bacteriocide	production of substances inhibiting pathogens growth: antibiotics, toxins, biosurfactants
Fungi	*Akantomyces muscarius* (formerly *Lecanicillium muscarium*)	insecticide	penetration and multiplication into the insect, causing death of the pest
	Ampelomyces quisqualis	fungicide	penetration and attack of the pathogens, degrading the cytoplasm leading to fungal death
	Aureobasidium pullulans	fungicide	microbial antagonist of fungal pathogens, production of antifungal enzymes (chitinase, glucanase), competing for nutrients, and induction of natural resistance of a host
	Beauveria bassiana	insecticide	mycelium mechanical penetration into the insect, causing loss of water and nutrients from the pest body
	Clonostachys rosea	fungicide, insecticide	hyperparasitism, secretion of enzymes
	Coniothyrium minitans	fungicide	mechanical penetration of the colonized fungus by dissolving its plasma walls, thus creating sources of infection
	Gliocladium catenulatum	fungicide	secretion of chemical substances inhibiting growth of other fungi, competing for space and nutrients
	Isaria fumosorosea	insecticide	hyperparasitism – production of enzymes disrupting insect growth and mechanical penetration of the insect body
	Metarhizium anisopliae	insecticide	attack on haemolymph by penetrating insect's epidermis resulting in loss of nutrients, physical disability and infection of the pest organs
	Phlebiopsis gigantea	fungicide	creating a natural coating on the cut or injured part of plant, preventing the invasion of pests
	Paecilomyces fumosoroseus	insecticide	spores act on a contact and germination on cuticle of insects
	Pythium oligandrum	fungicide	microbial antagonist of fungal pathogens, increase of plant resistance
	Purpureocillium lilacinum	insecticide, nematicide	secretion of the enzyme – chitinase, penetration the nematode egg shell
	Trichoderma afroharzianum	fungicide	inhibition of growth of pathogenic fungi by competing for nutrients and invasion sites, secretion of antifungal substances

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Table 1 to be continued

Type	Active substance	Agent type	Mode of action**
Fungi	*Trichoderma asperellum*	fungicide	competing for space and nutrients, mycoparasitism, production of enzymes able to degrade fungal cell walls, production of other antifungal substances and stimulation of the plant immune system
	Trichoderma atroviride	fungicide	competing for nutrients and space
	Trichoderma gamsi	fungicide	competing for space or nutrients, mycoparasitism, and secretion of enzymes able to degrade cell walls of parasites, production of antifungal substances, solubilization of inorganic components, and stimulation of the plant immune system
	Trichoderma harzianum	fungicide	parasitism, production of antibiotic substances (particularly, at low pH), competing for nutrients, secretion of enzymes dissolving the cell wall and enabling penetration into the host mycelium
	Verticillium albo-atrum	fungicide	induction of natural mechanisns of plant resistance
Yeasts	*Candida oleophila*	fungicide	competing for space and nutrients
	Cerevisane – a component of *Saccharomyces cerevisiae* cell wall	fungicide	induction of natural mechanisms of plant resistance
	Metschnikowia fructicola	fungicide	competiting for space and nutrients, secretion of chitinolytic enzymes
Viruses	*Cydia pomonella* granulosis virus	insecticide	insect tissues infected by the virus – reduced resistance to bacterial and fungal diseases
	Helicoverpa armigera nucleopolyhedrovirus	insecticide	on ingestion the virus invades the insects body, multiply leading to death
	Pepino mosaic virus	resistance inducer	virus inoculation for cross protection
	Spodoptera littoralis nucleopolyhedrovirus	insecticide	following ingestion the virus multiplies inside the insects body leading to death
	Granulovirus infecting the summer fruit tortrix (*Adoxophyes orana)*	insecticide	insect tissues infected by the virus – reduced resistance to bacterial and fungal diseases
Inorganic compounds	iron(III) phosphate	molluscicide	reduction of mucus secretion by snails; impact on calcium metabolism in slugs and snails intestine, so they stop feeding
	copper in form of copper oxychloride, tribasic copper(II) sulfate, copper(II) hydroxide	fungicide, bacteriocide	replacement of certain cations in the chitin wall (hydrogen, calcium, magnesium) with copper ions, contamination of structural and enzymatic proteins of the cell membrane – blocking of spore germination
	potassium hydrogen carbonate	fungicide, insecticide	changing conditions of the pest development by increasing the leaf surface alkalinity and the osmotic pressure on the plant surface
	sulphur	fungicide	penetrating into fungal cells through a cell membrane disrupting the osmoregulation process leading to fungal death, disrupted energy production in fungal cells
	azadirachtin A	insecticide	disrupting insect development at the pre-imago stage, inhibition of production and secretion of ecdysone, the main insect moulting hormone, repelling effect
	COS-OGA – chitooligosaccharides obtained by depolymerisation of natural chitosan and oligogalacturonides derived from natural pectins	immunity stimulator	induction of natural mechanisms of plant resistance
	green mint oil extract	growth regulator	disrupts potato sprouting by inhibiting cell growth
	ethylene	growth regulator	regulation of plant growth, development and death processes, stimulating fruit ripening
	fatty acids	insecticide, acaricide	mechanical penetration of the insect body disrupting osmoregulation and gas exchange

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Table 1 to be continued

Type	Active substance	Agent type	Mode of action**
Inorganic compounds	laminarin	immunity stimulator	stimulation of natural mechanisms of plant resistance
	paraffin oil	insecticide, acaricide	mechanical penetration of the insect body through stigmas resulting in their blocking, and in consequence, the insect death through asphyxiation, repelling effect on numerous phytophages
	orange oil	insecticide, fungicide	drying of cell walls in mycelium and spores
	rape seed oil	insecticide	forming a biofilm on the pest body surface, resulting in asphyxiation of insects and mites
	quartz sand	repellent	mechanical action, disruption by destroying insect mouthparts, and cuticle
	pyrethrins	insecticide	attacking insect nervous system, loss of movement coordination – paralysis
	sheep fat	repellent	repelling wild game with scent and flavour
	aliphatic acetate compounds	attractant	a pheromone attracting males of controlled insects

*EU Pesticides Database – https://ec.europa.eu/food/plants/pesticides/eu-pesticides-database_en

**BPDB (2022); Ciesielska et al. (2011)

review concerning the decomposition of pesticide residue indicates great interest in the use of biological methods for the degradation of active substances by bacteria, fungi, and yeasts.

Bacteria. In the case of bacteria, the biodegradation of pesticides is most frequently observed in bacteria from the *Bacillus* spp. genus. Their biodegradation ability results from the production of extracellular enzymes that act on a broad array of organic compounds (Bass & Field 2011). Enzymes participating in the biodegradation of pesticides by *Bacillus* spp. include: laccase, esterase (Gangola et al. 2018), hydrolase (Narayanan et al. 2020), carboxylesterases (Khan et al. 2016), and organophosphate hydrolase (Acharya et al. 2015). The largest number of studies focused on *Bacillus subtilis*.

The studies were concerned with the degradation of pesticides by four *B. subtilis* strains: DR-39, CS-126, TL-171 and TS-204 isolated from grapevines or the grape rhizosphere, analysed in a liquid culture, on grape berries and in vineyard soil. Each one of the four *B. subtilis* strains enhanced the degradation of profenofos in all three matrices. The results indicate that all four *B. subtilis* strains were able to degrade profenofos even when other carbon sources were available in the medium, at a level of 90% (TS-204, TL-171, CS-126) or 79% (DR-39), as compared to 52% degradation observed in the uninoculated control. The kinetics of the *in vitro* profenofos degradation showed that the half-life decreased from 12.90 days in the uninoculated spiked control to < 4.03 days in the presence of the *B. subtilis* strains (Salunkhe et al. 2013).

The *B. subtilis* KPA-1 strain was studied for the degradation of monocrotophos. It was demonstrated that the biodegradation of that pesticide is performed by the enzyme, phosphorus-organic hydrolase, resulting in 94.2% degradation of the monocrotophos in the soil in aerobic conditions (Acharya et al. 2015).

The process of quinalphos degradation by *B. subtilis* was optimised by Gangireddygari et al. (2017a). The maximum degradation of quinalphos (78.7%) was observed at a pH of 7.5 and an optimum temperature of 35–37 °C. Additional carbon (glucose) and nitrogen (yeast extract) sources marginally improved the rate of the quinalphos degradation (Gangireddygari et al. 2017a).

Other studies concerned with the *B. subtilis* 1D strain impact on the cypermethrin degradation. Under optimised growth conditions, the bacteria achieved cypermethrin degradation at a level of 95% after 15 days. The end products of the cypermethrin biodegradation under aerobic conditions were cyclododecylamine, phenol, 3-(2,2-dichloroethenyl)-2,2-dimethyl cyclopropane carboxylate, 1-decanol, chloroacetic acid, acetic acid, cyclopentan palmitoleic acid, and decanoic acid. This bacterium uses the enzyme lactase in the metabolic pathway of the cypermethrin degradation. The strain utilises cypermethrin as the sole source of carbon for its growth, which suggests

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Table 2. Review of the literature on synthetic pesticide degradation by natural and biological active substances

Type	Active substance	Degradation, references
Bacteria	*Bacillus amyloliquefaciens*	acibenzolar-*S*-methyl – 5.4–5.7 times faster degradation; metribuzin – 8–18%; napropamide – 9–11%; propamocarb hydrochloride – 15–36%; thiamethoxam – 11–22% (72 h) (Myresiotis et al. 2012)
		cypermethrin – 45% (5 days) (Lee et al. 2016)
		phoxim – 96.1% (48 h) (Meng et al. 2019a)
		chlorpyrifos – 18.7%; dichlorvos – 53%; dipterex – 5.5%; phoxim – 68.3%; triazophos – 96.3% (1 h) (Meng et al. 2019b)
		carbendazim – 41.8% (6 days) (Li et al. 2019)
	Bacillus firmus	fipronil – 100% (Mandal et al. 2014)
	Bacillus pumilus	acibenzolar-*S*-methyl – 5.4–5.7 times faster degradation; metribuzin – 8–18%; napropamide – 9–11%; propamocarb hydrochloride – 15–36%; thiamethoxam – 11–22% (72 h) (Myresiotis et al. 2012)
		chlorpyrifos and its metabolite product TCP – 90% (8 days) (Anwar et al. 2009)
	Bacillus subtilis	profenofos – 79–90% (Salunkhe et al. 2013)
		monocrotophos – 94.2% (Acharya et al. 2015)
		quinalphos – 78.7% (2 days) (Gangireddygari et al. 2017a)
		dimethomorph – 83.3–85.7% (15 days); 85.8–90.9% (30 days); carbendazim – 78.8–84.2% (15 days); 84.1–88.1% (30 days); thiophanate methyl – 88.9–94% (15 days); 98.3–98.9% (30 days); hexaconazole – 66.2–67.8% (15 days); 79.4–84.1% (30 days); tetraconazole – 79.3–83.9% (15 days); 94.6–95.2% (30 days); myclobutanil – 76.6–79.6% (15 days); 95.7–99.8% (30 days); buprofezin – 64.7–81.7% (15 days); 74.5–86.7% (30 days); benzoate emamectrin – 75.9–84% (15 days); 100% (30 days) (Suryawanshi et al. 2018)
		penthiopyrad – 5% (14 days) (Podbielska et al. 2020)
		acibenzolar-*S*-methyl – 5.4–5.7 times faster degradation; metribuzin – 8–18%; napropamide – 9–11%; propamocarb hydrochloride – 15–36%; thiamethoxam – 11–22% (72 h) (Myresiotis et al. 2012)
		cypermethrin – 95% (15 days) (Gangola et al. 2018)
		boscalid – 52%; pyraclostrobin – 41% (Podbielska et al. 2018)
	Bacillus thuringiensis	fipronil and its metabolites (Mandal et al. 2013)
		malathion – 50% (3 days) (Kamal et al. 2008)
		quinalphos (Gangireddygari et al. 2017b)
	Pseudomonas spp.	aldrin, chlorpyrifos, coumaphos, DDT, diazinon, endosulfan, endrin, hexachlorocyclohexane, parathion-methyl, monocrotophos, parathion (Huang et al. 2018)
		chlorpyrifos – 87% (20 days); 92% (30 days); atrazine, parathion, carbofuran (Gilani et al. 2016)
		endosulfan – 100% (12 days) (Jesitha et al. 2015)
		aldrin – 43% (12 days) (Doolotkeldieva et al. 2018)
		pentachlorophenol – 70%; chlorpyrifos – 75% (Arunachalam & Velmurugan 2010)
		quinalphos – 90.4% (Pawar & Mali 2014)
		permethrin, cypermethrin – 90% (15 days) (Mendoza et al. 2011)
		endosulfan – 50% (3 days) (Shivaramaiah & Kennedy 2006)
		diazinon – 83.6% (14 days) (Essa et al. 2016)
	Streptomyces spp.	diuron – 95% (5 days); 100% (10 days) (Castillo et al. 2006); cypermethrin – 100% (24–30 h) (Lin et al. 2011); β-cypermethrin – 23–37.5%; 73.1% (24 h) (Chen et al. 2012); lindane – 50–80% (20 h) (Benimeli et al. 2006); chlordane – 99.8% (24 h) (Cuozzo et al. 2012); chlorpyrifos – 90% (24 h) (Briceno et al. 2012); carbofuran – 66.5–95.3% (10 days) (Jayabarath et al. 2010); alachlor – 60–75% (14 days); 50% (7 days) (Sette et al. 2004; Sette et al. 2005); aldrin – 90% (72 h) (Benimeli et al. 2003); methoxychlor – 40–76% (28 days) (Bourguignon et al. 2014); diazinon – 10.8–31.7%; 13–61.7% (Briceno et al. 2016)

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Table 2 to be continued

Type	Active substance	Degradation, references
Fungi	*Aureobasidium pullulans*	chlorobenzoate herbicides (Rajendran & Gunasekaran 2006)
	Metarhizium anisopliae	diazinon – 68.2–85.6%; profenofos – 54.7–63.7%; malathion – 83.8–91% (20 days) (Abd El-Ghany & Masmali 2016)
		chlorpyrifos, cypermethrin > 80% (21 days) (Ong et al. 2019)
	Purpureocillium lilacinum	glyphosate – 80% (7 days) (Spinelli et al. 2021)
	Trichoderma atroviride	dichlorvos – 56.7% (24 h) (Sun et al. 2001)
		dichlorvos – 96% (Tang et al. 2009)
		carbendazim – 21% (5 days) (Sharma et al. 2016)
	Trichoderma harzianum	carbendazim – 85% (5 days) (Sharma et al. 2016)
		chlorpyrifos, ethion – 70–80% (21 days) (Harish et al. 2013)
		chlorpyrifos – 97.9% (10 days) (Jayaraman et al. 2012)
		DDT – 83%; dieldrin – 74%; endosulfan – 61%; pentachloronitrobenzene (PCNB) – 52%; pentachlorophenol (PCP) – 12% (Katayama & Matsumura 1993)
		chlorfenvinphos – 60% (165 days) (Oliveira et al. 2015)
		clomazone – 24.2%; fluazifop-*P*-butyl – 24.8%; metribuzin – 23.5% (Szpyrka et al. 2020)
		carbofuran – 81.5% (14 days) (Afify et al. 2012)
		bromoxynil – 45.6–60.3% (3 days) (Askar et al. 2007)
		oxamyl – 72.5% (10 days) (Afify et al. 2013)
		pentachlorophenol – 100% (7 days) (Vacondio et al. 2015)
		penthiopyrad – 34.2% (3 days); 56.9% (14 days) (Podbielska et al. 2020)
		boscalid – 52%; pyraclostrobin – 41% (Podbielska et al. 2018)
		diazinon – 84.8–91.8%; profenofos – 71.1–84.0%; malathion – 90.6–91.8% (20 days) (Abd El-Ghany & Masmali 2016)
Yeasts	Cerevisane – a component of *Saccharomyces cerevisiae* cell wall	azoxystrobin, pyraclostrobin, iprodione, boscalid (Wołejko et al. 2016)
		glyphosate – 21% (24 h) (Low et al. 2005)
		thiram (Kitagawa et al. 2002)
		atrazine, terbuthylazine (Hack et al. 1997)
		pirimiphos-methyl – 48.8% (72 h) (Đorđević & Đurović-Pejčev 2016)
Inorganic compounds	copper	cypermethrin $t_{1/2}$ 115.5 min → $t_{1/2}$ 9.0 min; cyhalothrin $t_{1/2}$ 173.3 min → $t_{1/2}$ 115.5 min (Liu et al. 2007)
		lambda-cyhalothrin $t_{1/2}$ 182.4 → $t_{1/2}$ 59.2 (Rafiq et al. 2012)
		chlorpyrifos, chlorpyrifos-methyl (Blanchet & St-George 1982)

the adaptation of *B. subtilis* to the oligotrophic environment (Gangola et al. 2018).

The disappearance of boscalid and pyraclostrobin residue in apple fruit was investigated using an organic fertiliser enriched with strains of the antagonistic microorganisms *Bacillus* spp., *Trichoderma* spp. and mycorrhizal fungi *Glomus* spp. The residue levels of boscalid and pyraclostrobin were reduced by 52% and 41%, respectively, versus the control. This organic fertiliser simulates plant growth and development, improves the soil fertility, and promotes the healthy growth of roots and the above ground parts of plants. In orchards, it increases the plants natural resistance, improves the quality of the fruit during storage, and reduces the levels of chemical plant protection product residue (Podbielska et al. 2018).

Suryawanshi et al. (2018), in 2017–2018, conducted extensive research on the influence of the *B. subtilis* DR-39 formulation on enhancing the pesticide degradation in grapes, for dimethomorph, carbendazim, thiophanate methyl, hexaconazole, tetraconazole, myclobutanil, buprofezin, and emamectin benzoate. They demonstrated that the degradation was similar throughout those years; however, a faster degradation rate was observed during the initial

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period of 15 days, versus the period of 15–30 days. The application of *B. subtilis* DR-39 at a dose of 2.5 g/L reduced the calculated half-life of the pesticides by 1–3 days, except for buprofezin and hexaconazole, where it was reduced by 5 and 6.5 days, respectively, in 2016–2017, and for hexaconazole, with a reduction by 6 days in 2017–2018. Studies show that *B. subtilis* DR-39 applications in vineyards can be utilised for the faster degradation of multi-class pesticide residue (Suryawanshi et al. 2018).

The interactions of *B. subtilis* GB03, *B. subtilis* FZB24, *B. amyloliquefaciens* IN937a and *B. pumilus* SE34 with acibenzolar-*S*-methyl, metribuzin, napropamide, propamocarb hydrochloride and thiamethoxam at two concentrations in a liquid culture and in soil microcosm were studied. The 72-h studies showed that the degradation of acibenzolar-*S*-methyl at low (1.0 mg/kg) and high (10.0 mg/kg) concentrations was 5.4 and 5.7 faster, respectively, versus the control. The interactions between those species also influenced the degradation of metribuzin (8–18%), napropamide (9–11%), propamocarb hydrochloride (15–36%), and thiamethoxam (11–22%) (Myresiotis et al. 2012).

The bacterial strain *B. pumilus* C2A1 isolated from the soil can degrade chlorpyrifos and its hydrolysis metabolite 3,5,6-trichloro-2-pyridinol (TCP). The research was conducted under different culture conditions: pH, inoculum density, presence of added carbon/nutrient sources and pesticide concentrations. The pesticide was utilised by the microorganisms as the sole source of carbon and energy. The maximum pesticide degradation was observed at a high pH (8.5) and a high inoculum density. The strain C2A1 showed 90% degradation of TCP (300 mg/L) within 8 days of incubation (Anwar et al. 2009).

Furthermore, the influence of *B. amyloliquefaciens* on the degradation of other pesticides was studied. Lee et al. (2016) demonstrated the cypermethrin degradation at a level of 45% in 5 days, using the *B. amyloliquefaciens* APO1 strain in the mineral medium. Furthermore, when 2% glucose was added to the medium, the rate of cypermethrin degradation by the AP01 strain increased to about 60%. Therefore, AP01 may serve as a promising strain in the bioremediation of soils polluted with cypermethrin (Lee et al. 2016).

Meng et al. (2019a) demonstrated the phoxim degradation at a level of 96.1% using the *B. amyloliquefaciens* YP6 strain. The bacterium uses phoxim as the sole source of phosphorus. The optimum biodegradation conditions were 40 °C, a pH of 7.20, and an inoculum size of 4.17% (v/v) (Meng et al. 2019a).

To expand the range of biodegrading enzymes, alkaline phosphatase (AP3): from *B. amyloliquefaciens* YP6 was characterised and used to test its effectiveness in the degradation of five phosphorus-organic pesticides. AP3 reached its optimal activity at 40 °C and a pH of 10.3. The study was conducted for 1 h, revealing the biodegradation of 96.3% of triazophos, 68.3% of phoxim, 53% of dichlorvos, 18.7% of chlorpyrifos and 5.5% of dipterex (Meng et al. 2019b).

Another enzyme that can biodegrade pesticides is hydrolase HY-1 from *B. amyloliquefaciens.* Studies were performed in food, and it was demonstrated that this enzyme degraded 41.8% of carbendazim from the cucumber surface during a 6-day study (Li et al. 2019).

B. thuringiensis is another bacterium from the *Bacillus* spp. genus, responsible for the degradation of pesticides. The *B. thuringiensis* isolate (MOS-5) was evaluated during the incubation time of 30 days. The removal of a considerable amount of malathion after three days of incubation was observed. For instance, in an inoculated salt media, more than 50% of malathion was degraded to other compounds. After one week of incubation, the residual malathion levels decreased to 26.5% and reached 0.68% after 30 days of incubation. MOS-5 was able to utilise malathion as the sole carbon and energy source and to degrade it cometabolically (Kamal et al. 2008).

B. thuringiensis was used in studies on quinalphos degradation. It was studied whether an additional source of carbon and nitrogen, the inoculum density, pesticide concentration, pH and the temperature influenced the level of the pesticide degradation. The maximum degradation of quinalphos was observed with an inoculum of 1.0 optical density (OD), an optimum pH (6.5–7.5), and an optimum temperature of 35–37 °C (Gangireddygari et al. 2017b).

B. firmus can degrade fipronil under laboratory conditions. Soil samples were fortified with fipronil at concentrations of 0.50–1.50 mg/kg and inoculated with *B. firmus* cells. The study was conducted for 56 days. Pesticide residue was not detected after 35 days at lower doses of fipronil (0.50, 0.75, 100 mg/kg), and at higher concentrations (1.25 and

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1.50 mg/kg), and the pesticide had completely degraded after 42 days (Mandal et al. 2014).

Several reports are available concerning the influence of bacteria from the *Pseudomonas* spp. genus on pesticide residue. *Pseudomonas* spp. is a diversified genus with a great deal of catabolic pathways and enzymes involved in pesticide degradation. In the case of chlorpyrifos, *Pseudomonas* was found to have a high degradation potential due to the widespread environmental adaptability, and it was followed by *Agrobacterium* and *Bacillus* (Abo-Amer 2012; Gilani et al. 2016).

Enzymes participating in the pesticide biodegradation by bacteria from the *Pseudomonas* genus include: oxidoreductases (Gox), cytochrome P450, dioxygenases (TOD), phosphotriesterases, and carboxylesterases (Ortiz-Hernandez et al. 2013; Saafan et al. 2016).

Pseudomonas ATCC 700113 degraded chlorpyrifos by reductive dechlorination to 3,5,6-trichloro-2-pyridinol (TCP) and then to carbon dioxide, water, chloride and ammonium (Feng et al. 1998). The chlorpyrifos degradation was noted at a level of 87% after 20 days and of 92% after 30 days (Gilani et al. 2016). *Pseudomonas* exhibits maximum degradation at a pH of 8 because at a high pH, enzymes have optimum activity and are able to degrade chlorpyrifos (Swetha & Phale 2005). *Pseudomonas* is adapted the best to low pesticide concentrations. The degradation of chlorpyrifos decreases with an increase in its concentration because the high concentrations affect the microorganisms involved in the degradation. Li et al. (2007) reported that when the concentration exceeds 200 mg/L, bacteria grow slowly and also stop degrading the intermediate TCP, while they function normally at low concentrations (Li et al. 2007).

P. fluorescens was studied for the degradation of endosulfan. It was demonstrated that this bacterium uses the pesticide as the sole source of carbon and energy. Endosulfan was completely degraded after 12 days. The formed metabolites implied that this pesticide is decomposed by hydrolysis (Jesitha et al. 2015).

In the studies on aldrin degradation by *P. fluorescens*, it was demonstrated that this microorganism degrades the pesticide using cytochrome P450 hydroxylase. The studied bacterium degraded 43.2% of aldrin during the 12-day study (Doolotkeldieva et al. 2018).

The level of the quinalphos degradation by *Pseudomonas* species isolated from the grape rhizosphere soils was determined. A total number of 14 *Pseudomonas* strains were isolated and screened for their tolerance to four concentrations of quinalphos (5 mg/L, 10 mg/L, 15 mg/L and 20 mg/L). The results indicated that only one strain could degrade the highest concentration of quinalphos at a level of 15 mg/L and 20 mg/L. The results showed that the isolated strain could degrade quinalphos at a level of up to 90.4% in the presence of glucose, and of up to 38.2% in the absence of glucose. This finding may be related to the role of glucose as an inducer of organism growth (Pawar & Mali 2014).

P. aeruginosa was isolated from agricultural drainage ditches (Fayoum, Egypt). A pure culture of *P. aeruginosa* was grown in a minimal medium supplemented with diazinon as the sole carbon source. The temperature and pH influence on the bacterial growth and the rate of diazinon degradation were investigated. The maximum diazinon degradation capability (83.6%) was achieved at a pH value of 7.0 and a temperature of 30 °C within 14 days (Essa et al. 2016).

P. putida and *P. mendocina* strains have great capacity for biodegrading permethrin and cypermethrin pesticides. The bioremediation of up to 90% can be achieved with the help of these bacterial strains within a period of 15 day (Mendoza et al. 2011).

Pseudomonas bacteria can degrade endosulfan. Endosulfan is metabolised into endosulfan sulfate, which is the only product of the endosulfan metabolism by bacteria. It resulted in 50% degradation of endosulfan within three days (Shivaramaiah & Kennedy 2006).

There are several reports of the effect of bacteria from the *Streptomyces* spp. genus on pesticide residue. *Streptomyces* spp. are able to remove organic and inorganic pollutants, such as: hydrocarbons, pesticides, aliphatic and aromatic compounds, making them good tools for the bioremediation process (Sambasiva Rao et al. 2012). Microorganisms represent an efficient source of oxidoreductases and hydrolytic enzymes. Amylases, protease, cellulase, xylanase, esterase, nitrile hydratase, laccase, dehydrogenase are some enzymes that could be involved in the pesticide degradation (Kariga & Rao 2011). *Streptomyces* spp. have the ability to grow and degrade several chemical families of pesticides, including: organochlorines, organophosphates, pyrethroids, ureas and chloroacetanilides (Briceno et al. 2013; Alvarez et al. 2017).

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Sette et al. (2004) and Sette et al. (2005) isolated 53 *Streptomyces* strains from alachlor contaminated soils. Sixteen strains were able to grow at a high pesticide concentration (720 mg/L) and six strains were able to degrade over 50% (72 mg/L) of alachlor from a mineral salt medium after 7 days (Sette et al. 2004; Sette et al. 2005).

Castillo et al. (2006) studied the biodegradation of diuron by 17 strains of *Streptomyces* spp. isolated from soils. All the strains were able to degrade the pesticide, but to different levels. Twelve strains degraded the herbicide by up to 50% and four of them by up to 70%. The study was conducted in a medium with 4 mg/L of diuron. *S. albidoflavus* A7-9 was the most efficient microorganism in the degradation of diuron, achieving 95% degradation after five days and no herbicide residue after 10 days (Castillo et al. 2006).

Lin et al. (2011) isolated *Streptomyces* sp. HU-S-01 from wastewater sludge and studied the degradation of cypermethrin by this microorganism. At pesticide concentrations lower than 50 mg/L, the strain completely degraded cypermethrin within 30 hours. At higher concentrations – 150–250 mg/L, the degradation of the pesticide was incomplete even after 48 h of incubation. The optimum degradation condition was at a temperature of 26–28 °C and a pH of 7.5. The influence of *Streptomyces* sp. HU-S-01 on the degradation of the major metabolite, 3-phenoxybenzoic acid (3-PBA), of cypermethrin hydrolysis in soil and water was also investigated. HU-S-01 completely degraded 3-PBA at a concentration 50 mg/L, but the degradation rate of the metabolite was slower than cypermethrin. Complete degradation occurred after 96 hours (Lin et al. 2011).

The degradation of chlorpyrifos (CP) by *Streptomyces* spp. isolated from agricultural soil was investigated. Two strains were selected because of their tolerance to 50 mg/L of CP. *Streptomyces* sp. AC5 and *Streptomyces* sp. AC7 were cultivated in a medium with CP at concentrations of 25 mg/L and 50 mg/L for 72 hours. Both strains were able to degrade CP with about 90% degradation after 24 hours. *Streptomyces* sp. AC5 degrade CP into 3,5,6-trichloro-2-pyridinol (TCP) reaching the maximum metabolite concentration of 0.46 mg/L, while the concentration of TCP was 1.31–4.32 mg/L for *Streptomyces* sp. AC7 (Briceno et al. 2012).

Another study was concerned with the degradation of carbofuran by three isolates: *S. alanonosinicus*, *S. album* and *S. atratus*, which were able to resist the pesticide and showed growth on a medium with a pesticide concentration of 20 µg/L. After 10 days, 65.5%, 64.9% and 34.8% of carbofuran was degraded by *S. alanonosinicus*, *S. atratus* and *S. album*, respectively (Jayabarath et al. 2010).

Bourguignon et al. (2014) isolated *Streptomyces* strains from pesticide-contaminated sediments. The microorganisms were able to grow in the presence of 1.66 mg/L of methoxychlor (MTX). The MTX degradation by *Streptomyces* sp. A14 was at level of 40% and 76% for the pesticide concentrations of 8.33 and 16.6 mg/kg (28 days), respectively. *Streptomyces* sp. A14 showed the best growth in the presence of MTX in the culture medium at 30 °C and a pH of 7 (Bourguignon et al. 2014).

Fungi. Fungi generally biotransform pesticides and other xenobiotics by introducing minor structural changes to the molecule, rendering it nontoxic. The biotransformed pesticide is released into the environment, where it is susceptible to further degradation by bacteria (Diez 2010).

Fungi tolerate high levels of pollutants better than bacteria (Evans & Hedger 2001). With characteristics such as specific biodegradation and/or growth morphology, fungi degrade the pollutants more effectively (Mollea et al. 2005).

Three possible mechanisms for pesticides degradation by fungi have been proposed: (1) the pesticide is used as a source of carbon or nitrogen by capture or extracellular decomposition of a compound; (2) cometabolism effected by enzymes secreted by the fungi, in which the pesticide is not used by a given fungus as a source of carbon and energy; (3) a detoxication mechanism in fungi exposed to toxic compounds (Ellegaard-Jensen 2012).

The fungi use enzymes such as extracellular oxidases and peroxidases, including laccases, manganese peroxidases, aryl alcohol oxidases, and lignin peroxidase, for the biodegradation of pesticides (Paszczyński & Crawford 2000; Novotny et al. 2004).

Fungi from the *Trichoderma* spp. genus are the most popular biocontrol agents (BCAs) known worldwide for their great ability to combat different soil and foliar diseases of agricultural crops. *Trichoderma* spp. are used in biopesticides because of their ability to destroy other fungi, induce resistance to plant pathogens, improve plant growth, solubilise plant nutrients, and bioremediate heavy metals and environmental pollutants, such as pesticides (Szpyrka et al. 2020). For the biodegradation

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of pesticides, *Trichoderma* spp. use mechanisms such as nutrient competition, antibiosis, the activity of cell wall-lytic enzymes, the induction of systemic resistance, and increased plant nutrient availability (Ene & Alexandru 2008). In studies on biodegradation of pesticides, the researchers' attention has been drawn to a species of fungi, *Trichoderma harzianum*.

Another study was concerned with the impact of *T. harzianum* and *Rhizopus nodosus* isolated from the contaminated soil on the degradation of two phosphorus-organic pesticides, chloropyrifos and ethion. The fungi were able to degrade 70–80% of the pesticides within 21 days of the incubation period. Furthermore, the degradation efficiency increased by 10–20% with the supplementation of 0.1% dextrose to the mineral media (Harish et al. 2013).

The *T. harzianum* influence on the decomposition of five pesticides: DDT, dieldrin, endosulfan, pentachloronitrobenzene (PCNB), and pentachlorophenol, was demonstrated, with a degradation level of 83%, 74%, 61%, 52%, and 12%, respectively. The discussed publication focused, in particular, on endosulfan degradation. The initial metabolic product of the endosulfan decomposition was endosulfan sulfate, and the oxidative system is the major enzyme system in *T. harzianum* responsible for the endosulfan degradation (Katayama & Matsumura 1993).

Another study was concerned with the degradation of several pesticides exposed to a mixture of fungi: *Penicillium citrinum, Aspergillus fumigatus, A. terreus* and *T. harzianum*, found in the aquatic environment. The analyses were conducted for 165 days and demonstrated that those microorganisms are able to degrade 60% of chlorfenvinphos, versus the control (Oliveira et al. 2015).

The influence of the commercially available biological fungicide containing *T. harzianum* Rifai T-22 on the dispersion and degradation kinetics of five herbicides: clomazone, fluazifop-*P*-butyl, metribuzin, pendimethalin and propyzamide, was studied in two types of soil. The study results showed that *T. harzianum* T-22 influences the degradation of pesticides and the dispersion kinetics of non-persistent herbicides: clomazone, fluazifop-*P*-butyl, and metribuzin. In the soil with a higher content of nitrogen, phosphorus and organic matter, the degradation increased by 24.2%, 24.8% and 23.5% for clomazone, fluazifop-*P*-butyl, and metribuzin, respectively. In the soil with a lower organic content, the degradation was at a low level, at 16.1%, 17.7% and 16.3% for clomazone, fluazifop-*P*-butyl, and metribuzin, respectively. The results obtained for more persistent pesticides: propyzamide and pendimethalin were not advantageous (Szpyrka et al. 2020).

Another area of investigation was the effect of gamma radiation on the carbofuran degradation by *T. harzianum*. The analysed pesticide was transformed into 3-ketocarbofuran. Fungus samples were collected and exposed to different doses of gamma radiation. Fungi from the 7-day-old culture were irradiated with doses of 0.0, 0.02, 0.05, 0.1, 0.25, 0.5, 1.0, 2.0, and 5.0 kGy. It was demonstrated that the radiation influenced the level of the pesticide degradation. During exposure to the gamma radiation, the carbofuran degradation by *T. harzianum* was at a level of 76.5% and 85% in sterile and non-sterile soils, respectively, during 14 days of incubation (Afify et al. 2012). These results were compared to earlier studies, where *T. harzianum* was not exposed to radiation, and the degradation was at a level of 75% and 81.5% in sterile and non-sterile soils, respectively, during 14 days of incubation (Afify & Shousha 1988).

Similar studies were also conducted on the influence of gamma radiation on the oxamyl decomposition. The results indicated that *Trichoderma* spp. used oxamyl as source of carbon and nitrogen, and had enzyme(s) acting on the amide and ester bond in the oxamyl structure. The oxamyl degradation by *T. harzianum* strain reached 72.5% within 10 days of incubation (Afify et al. 2013).

Furthermore, the *T. harzianum* influence on the bromoxynil decomposition was determined. The pesticide levels exposed to that fungus dropped to 45.61, 21.25, 20.63, 10.49, and 1.56 ppm after 3, 7, 14, 21, and 28 days of incubation, respectively (with an initial level of 100 ppm). Less than 2% of the initial concentration was detected after 28 days (Askar et al. 2007).

Vacondio et al. (2015) studied the degradation of pentachlorophenol (PCP) and its metabolite, 2,3,4,6-TeCA, by *T. harzianum* CBMAI 1677. After seven days, these compounds were completely decomposed. Enzymes, such as phenoloxidases and cellobiose dehydrogenase, operating simultaneously with ligninolytic enzymes degrade PCP (Vacondio et al. 2015).

The influence of *T. harzianum* on the degradation of phosophorus-organic pesticides: diazinon, profenofos and malathion, was studied for different pes-

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ticides concentrations, incubation periods and temperatures. *T. harzianum* degraded 91.8% (10 mg), 98.2% (20 mg) and 84.8% (40 mg) of diazinon within 20 days. Profenofos was degraded by 78.3%, 84.0% and 71.1% at concentrations of 10 mg, 20 mg, and 40 mg, respectively, after 20 days. In the case of malathion, 90.6%, 91.8% and 90.6% of its initial concentration were degraded within 20 days for the initial concentrations of 10 mg, 20 mg, and 40 mg, respectively. The optimal temperature for the pesticides degradation by *T. harzianum* is 35 °C. *T. harzianum* proved to be more effective in the degradation of those pesticides than *Metarhizium anisopliae* (Abd El-Ghany & Masmali 2016).

Furthermore, the influence of *T. harzianum, T. viride* and *T. atroviride* on the degradation of carbendazim in three concentrations of 100, 150 and 200 ppm was studied. After five days of incubation, the percentage biodegradation of carbendazim was 85% for *T. harzianum*, 47% for *T. viride*, and 21% for *T. atroviride* (Sharma et al. 2016).

The *T. atroviride* T23 strain was used to degrade dichlorvos. The pesticide was degraded in 56.7% to the following compounds: dichloroacetic acid, 2,2-dichloroethanol and phosphoric acid. The enzyme responsible for 2,2-dichlorovinyl dimethyl phosphate (DDVP) degradation was organophosphorus hydrolase. The highest activity of this enzyme was achieved at 35 °C, and the optimal pH was 8.5. The results showed that organophosphorus hydrolase provided a clue for the comprehensive understanding the mechanism underlying the organophosphorus pesticide degradation by filamentous fungi (Sun et al. 2001).

Other studies involved the application of *T. atroviride* transformants with the enzyme hygromycin B phosphotransferase to analyse the dichlorvos degradation. The transformants were characterised by an increased ability to degrade dichlorvos. Of 247 transformants, 76% showed improved a dichlorvos degradation ability when compared to the parent strain T23. Among them, eight transformants exhibited a 30% higher degradation rate than the parent isolate. The highest dichlorvos degradation rate achieved by the transformants was up to 96% (Tang et al. 2009).

Studies were also conducted on the influence of a fungus, *Metarhizium anisopliae*, on the degradation of pesticides, due to its ability to promote biological control in the environment, especially in crops. In was found that *M. anisopliae* shows high resistance to herbicides, acaricides and insecticides in the environment, so this fungus can be used together with chemical plant protection products to protect plants, and for further studies on the degradation of pesticides in the environment (Mochi et al. 2005).

The influence of *M. anisopliae* on the degradation of phosophorus-organic pesticides: diazinon, profenofos and malathion, was assessed for different pesticides concentrations, incubation periods and temperatures. The study results showed that profenofos, diazinon and malathion degradation increased with an increase in the incubation time, but, at the same time, decreased with an increase in the initial concentrations of those insecticides. *M. anisopliae* degraded 85.6% (10 mg), 77.2% (20 mg) and 68.2% (40 mg) of diazinon within 20 days. Profenofos was degraded at 54.7%, 62.4% and 63.7% at concentrations of 10 mg, 20 mg, and 40 mg, respectively, after 20 days. In the case of malathion, 89.2%, 91.0% and 83.8% of its initial concentration were degraded within 20 days for initial concentrations of 10 mg, 20 mg, and 40 mg, respectively. The optimal temperature for the pesticides degradation by *M. anisopliae* is 30 °C (Abd El-Ghany & Masmali 2016).

On the basis of the above studies, Ong et al. (2019) proposed the use of *M. anisopliae* for the biodegradation of two pesticides: cypermethrin and chlorpyrifos in the soil. The study was conducted for 21 days, and demonstrated that the degradation of those two insecticides exceeded 80% and was higher versus the control (47–61%). The chlorpyrifos and cypermethrin residues in *M. anisopliae* treated soils amounted to 19.39 ± 0.10 ppm and 19.68 ± 0.36 ppm, respectively, and were significantly lower than in the control (residue levels of 262.6 ± 7.6 ppm for chlorpyrifos and of 194.4 ± 4.3 ppm for cypermethrin, at $P < 0.05$) (Ong et al. 2019).

The literature review shows that only one research paper on the effect of a yeast-like fungus *Aureobasidium pullulans* on the degradation of pesticides has been published so far. *A. pullulans* is an effective agent for the biological control of storage diseases in many species of fruit, including apples (Castoria et al. 2001; Schena et al. 2003). Thus, an interest in further studies on the degradation of pesticides by this fungus may be stimulated (Vero et al. 2009). Rajendran and Gunasekaran (2006) found that *A. pullulans* degrades chlorobenzoic herbicides (Rajendran & Gunasekaran 2006).

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Yeast. Yeasts of the *Saccharomyces cerevisiae* species, whose cell wall is an active substance of biological plant protection agents, were also studied. *S. cerevisiae* is particularly active in the quick conversion of sugars into alcohol and carbon dioxide, thus contributing to the limited availability of nutrients for other organisms inhabiting the plant organs. Additionally, it is capable of producing so-called toxin killers which, as protein complexes, exhibit very strong inhibitory properties against the pathogens present in the same environment (Wołejko et al. 2016).

It was demonstrated that *S. cerevisiae* is responsible for the glyphosate degradation during the fermentation cycle of the breadmaking process, where 21% of the pesticide was degraded within 1 h (Low et al. 2005).

Other studies on *S. cerevisiae* concerned the degradation behaviour of pirimiphos methyl in wheat during fermentation. Yeast fermentation was especially effective for the reduction of pirimiphos methyl applied at 5 mg/kg (the maximum residue limit), causing a maximum dissipation of 48.8% (72 h). The pesticide reduction rate decreased with an increase in the fortification rate. Thus, in samples fortified with 25 and 75 mg/kg of the yeast, a reduction of up to 27.1%, and 23.7% was observed, respectively (Đorđević & Đurović-Pejčev 2016).

It was proven that the yeast *S. cerevisiae* is responsible for the biodegradation of*:* azoxystrobin, pyraclostrobin, iprodione, boscalid (Wołejko et al. 2016), thiram (Kitagawa et al. 2002), atrazine, and terbuthylazine (Hack et al. 1997).

Other. Following the literature review, it was found that studies on the influence of pesticide degradation were only conducted for copper among the inorganic and other substances used in biological and natural preparations.

Liu et al. (2007) analysed the effect of copper on cypermethrin and cyhalothrin in the soil and on their photodegradation in the aquatic system. In the soil, the degradation of pesticides was not accelerated. For the photodegradation, the half-life decreased from $t_{1/2}$ 173.3 min to $t_{1/2}$ 115.5 min for cyhalothrin, and from $t_{1/2}$ 115.5 min to $t_{1/2}$ 99 min for cypermethrin. The results suggested that copper influenced the degradation of the pesticides in the soil by affecting the activity of the microorganisms. However, it had a catalyst effect on the photodegradation in the water system. The difference was also observed for the efficiency of the degradation of the pyrethroid isomers in the soil. Copper could obviously accelerate the degradation of certain isomers (Liu et al. 2007; Wang et al. 2007).

The influence of copper on the photodegradation of two pesticides, imidacloprid and lambda-cyhalothrin, commonly used in cotton crops, was also investigated. For this purpose, different concentrations of pesticides were irradiated in a UV photoreactor with a wavelength of > 300 nm at different time intervals, i.e., 0–960 minutes. The Cu effect on photodegradation was studied, by adding Cu to the pesticide solution. After irradiation, the remaining concentrations of the pesticides were determined. The study showed that the photodegradation rate of lambda-cyhalothrin increased in the presence of Cu. This was confirmed by the reduction of the lambda-cyhalothrin half-time $t_{1/2}$, from 182.36 min to 59.2 min in the presence of Cu. On the contrary, the imidacloprid photodegradation is delayed after the addition of Cu. This was probably caused by the pesticide stabilisation through complexation with metal ions (Rafiq et al. 2012).

Furthermore, the influence of copper on chlorpyriphos and chlorpyriphos-methyl in buffered water solutions was demonstrated. As the concentration of copper(II) increased, the rate of hydrolysis increased until the concentration of copper(II) reached about 1.0×10^{-2} M. At this point, the rate of hydrolysis became independent of the copper(II) concentration. During the study on the pesticide degradation by copper, the presence of copper-pesticide complexes, an intermediate product in the hydrolysis reaction, was observed. The copper(II) ion forms a six-membered ring complex with nitrogen in the ring structure and sulfur of phosphorothioate moiety from the chlorpyrifos and chlorpyrifos–methyl (Blanchet & St-George 1982).

In Figure 1, the summary of the information included in Table 2 can be seen. All the microorganisms presented in this study, which have the potential of pesticide degradation are shown with the number of pesticides tested and their maximum degradation.

CONCLUSION

The use of natural and biological agents in environmental protection is associated with a number

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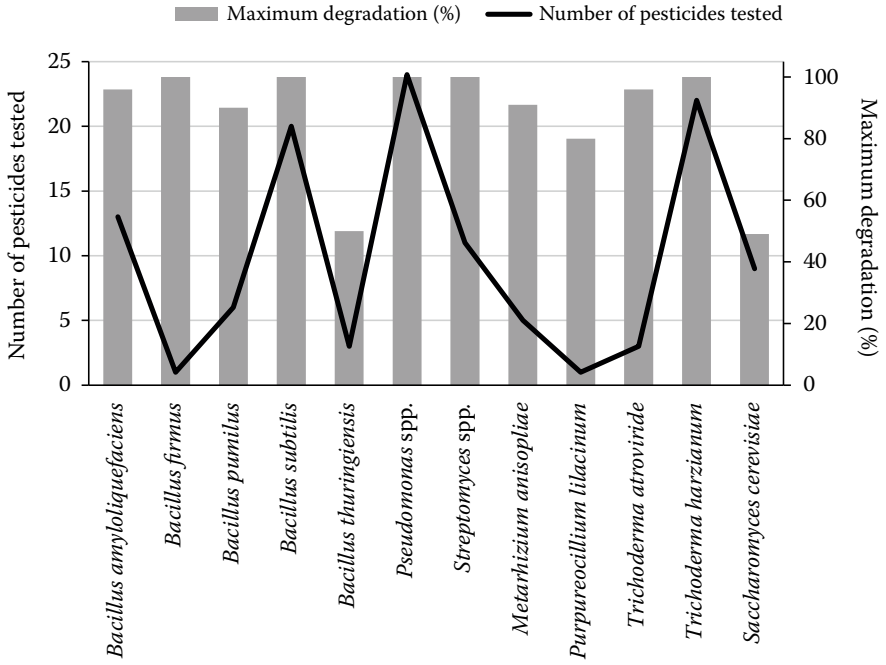

Figure 1. Number of pesticides tested and their maximum degradation (%) for the particular microorganisms

of advantages, including the prevention of pest resistance developing to chemical PPPs, an increase in the yield, an increase in the biodiversity, and the faster decomposition of toxic pollutants. The effects of these agents result, among other things, from the phenomenon of antibiosis, competing for space and nutrients, antagonism, and stimulation of host's natural resistance mechanisms. Biopesticides containing, e.g., microorganisms, are responsible for the degradation of pesticide residue in the environment. The most common mechanism underlying the biodegradation conducted by microorganisms is the decomposition of substances by enzymes secreted outside the cell, which degrade chemical compounds to their less toxic or non-toxic derivatives. The review of the literature on the biodegradation of pesticides by microorganisms implies a significant interest in this subject. The largest body of literature data concerns bacteria from the *Bacillus* spp. and *Pseudomonas* spp. genera, fungi from the *Trichoderma* spp. genus and the yeast *S. cerevisiae*. The most important and most perspective bacteria and fungi used in integrated pest management are *Bacillus* spp. and *Trichoderma* spp. because their effectiveness in pesticide degradation and the large number of commercial preparations containing these microorganisms available on the market. Application of biological pesticides recommended in integrated pest management programmes could significantly improve the quality of the soil, environment, and human health.

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