

Leonardo F. Fraceto

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Nanopesticides

From Research and Development
to Mechanisms of Action and
Sustainable Use in Agriculture



Springer

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ISBN 978-3-030-44872-1 ISBN 978-3-030-44873-8 (eBook)
<https://doi.org/10.1007/978-3-030-44873-8>

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The registered company address is: Gewerbestrasse 11, 6330 Cham, Switzerland

This book is dedicated to those who made remarkable scientific discoveries and imagined their applications that ameliorate our lives and promote environmental sustainability

Foreword

One of the growing interest areas of nanotechnology applications is the development of novel formulations of pesticides that are more efficient, targeted, and release controlled. Such features may not only bring about cost savings but may also lower the overall use of pesticides and thus contribute towards reducing the negative impacts on human health and the environment. However, despite the novelty of the approach, only a few research groups have so far ventured into this area of R&D due to the current major gaps in knowledge. This book will, therefore, be useful in enhancing the understanding of fundamental concepts, underlying mechanisms, and state-of-the-art regarding nanopesticides.

The book is comprised of 11 chapters that are written by leading experts in their respective fields. It takes an account of the cutting-edge of the technology, gives pointers to the future directions of R&D, and identifies the areas where further research is needed. In describing the new technology, the authors have taken a balanced view by highlighting both the likely benefits and the potential risks of formulating pesticides at the nano-scale. In particular, the nano-scale formulation of natural pesticidal compounds, together with biodegradable polymers, can open up numerous new possibilities for the development of safer products for the control of a variety of pests of agricultural and public health importance. The Experts' perspectives on the novelty, the future prospects and trends of the technology, and regulatory aspects will be equally informative for the developers, the regulators, and the users of nanopesticides.

In this context, Chap. 1 has looked into the use of natural degradable polyhydroxyalkanoates (PHAs) for the development of embedded extended-release formulations of herbicides and fungicides. It also provides example applications in laboratory soil ecosystems in wheat plant communities infected with *Fusarium sp.* and weeds.

Chapter 2 provides another interesting example of the development of smart formulations based on biodegradable and eco-friendly nano-chitosan and their application in fungal disease control.

The use of RNA interference (RNAi) is an interesting field of biotechnology that has also been studied for potential applications in pest control. However, such

applications generally suffer from limitations in the delivery of dsRNAs to diffused and dispersed pest populations in the field. This is where the use of nano-carriers has been studied as a delivery vehicle for RNAi-based pesticides for the control of agricultural pests. Chapter 3 presents an overview of the literature on this topic, and discusses biosafety considerations in relation to the use of formulations based on nano-carrier containing RNAi.

Chapter 4 is focused on discussing the interaction of nanopesticides with plants. Such an understanding is fundamentally important to drive effective, safe, and sustainable application of nanopesticides in agriculture. Whilst the discussion centres around the conceptual basis, it also provides different examples of the uptake, mode of action, and effects of nanopesticides in the context of physiological and metabolic responses of plants exposed to nanopesticides. It also demonstrates prediction models that can provide a hint on the likely response of the plants to a specific type of nanopesticide.

Chapter 5 discusses the methods that can be used to study the behaviour and fate of nanopesticides in aquatic and terrestrial environments. It discusses the advantages and disadvantages of individual methods and highlights the important considerations that are needed due to the nano-scale characteristics of nanopesticides when using conventional environmental risk assessment methods.

Chapter 6 continues the theme of Chap. 4 to further discuss the interactions of nano-enabled agrochemicals with soil microbiome that plays a vital role in maintaining the soil quality as well as plant nutrition and health. Using examples of formulations based on nano forms of copper and silver, as well as nanocarriers of conventional pesticides, the chapter discusses the current state of knowledge in regard to the potential prospects and implications of nanopesticides for the soil microbiota.

Chapter 7 discusses bioactivity and environmental impacts of nano-formulated insecticides. Whilst the comprehensive overview presented in this chapter includes nano-formulation of synthetic pesticides, a particular focus is also on formulations of natural insecticidal compounds, the use of which can be expected to further minimize the environmental impacts. A similar theme is discussed in Chap. 8 in relation to the environmental toxicity of nanopesticides against non-target organisms. The comprehensive state-of-the-art overview concerns environmental safety of nanopesticides against non-target model organisms (microbes, plants, worms, insects, algae, daphnids, and fish). It also touches upon the various methods for characterization for the study of interactions of nanopesticides with biological and environmental systems, the use of nano-informatics, safety-by-design, environmental risk analysis and management for responsible development and regulation of nanopesticides.

Chapter 9 provides an overview of the aspects relating to environmental safety and regulation. Using a case study of nano-atrazine, the chapter discusses the current limited knowledge in relation to the behaviour and fate, and the potential adverse environmental impacts of nanopesticide formulations. It not only takes a note of the new advancements but also highlights the main challenges in regard to risk analysis of nanopesticides. This theme is further elaborated in Chap. 10 that discusses risk assessment of nanofertilizers and nanopesticides. The review shows

that environmental and human health impacts of the nano-agrochemicals are of general concern. It highlights the scarcity of the relevant toxicological data to allow adequate risk assessment. The impact of the such knowledge gaps is considered a barrier to the development of regulatory policies, and, as a consequence, an obstacle to new marketable products.

Finally, Chap. 11 provides a market analysis of nanopesticides at different stages from R&D to the market. The market scenario depicts a continuous investment in the technology and innovation to develop more effective products, in a framework of mergers, ventures, and partnerships to accelerate the development and launch of the products. The analysis indicates that the development of nano-encapsulated pesticide formulations is currently an open field that can enable the development of new original materials and formulations. The overview identifies the current status and trends in the market, and provides a summary of the forthcoming technologies. It discusses the key challenges in the scale-up, and identifies encapsulation of microorganisms and dsRNA as new and emerging disruptive technologies.

In summary, the book provides an up-to-date account of the cutting-edge technology for the development of nanopesticides, its pros and cons, and potential applications in agriculture. It provides a balanced view of the innovations in this field in consideration of both benefits and risks. The book is highly commended to all those involved in R&D and safety/regulation of pesticides in an academic, research, industrial, or regulatory setting.

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Qasim Chaudhry

Preface

Nanomaterials have been contributing to agricultural science and technology in various phases of production and commercialization. Especially, nanopesticides can improve crop yields and are believed to reduce harmful effects on the environment. Their benefits may include better stability, permeability, and dispersion of the active ingredient, improved targeting to pest species, higher efficacy, decreased application doses, prevention of premature degradation, and increased environmental safety. Despite their promising use, it is necessary to study their accumulation in the environment and their impact on non-target organisms and consequently on biodiversity and human health. Nowadays, there is a lack of worldwide data on nanopesticide efficacy compared to conventional ones and on their environmental effects. Considering these facts, we discuss in this book some recent features of nanopesticide development, application, and toxicity evaluation. The book is organized into 11 chapters. Chapters 1–3 describe the use of different carriers for the controlled release of active ingredients aiming at agriculture applications. Chapters 4–6 describe some methods used to understand the fate and behaviour of nanopesticides in plants, soil, and water. Chapters 3 and 6 discuss their potential toxicity and impacts on the environment. Chapters 7 and 8 showed the potential toxicity of nanopesticides and their impacts on environment. Chapters 9 and 10 provide an overview of environmental safety aspects and regulatory issues regarding nanopesticides. Finally, Chapter 11 discusses the commercial aspects of nanopesticides in crop production.

In this context, with this book, we intended to contribute to a broader perspective of nanopesticide characteristics and risk assessment, regulation, application, and marketing.

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Acknowledgements

The editors would like to heartily acknowledge all authors for the valuable sharing of their findings, knowledge, and opinions in this book. Also, the editors would like to thank Springer for the opportunity to publish this book. In addition, we would like to thank Brazilian fellow agencies: São Paulo Research Foundation (FAPESP #2017/21004-5), CAPES, and CNPq (#306583/2017-8). We are also grateful to Prof. Qasim Chaudhry for his kind words in the foreword.

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Natural Degradable Polyhydroxyalkanoates as the Basis for Creation of Prolonged and Targeted Pesticides to Protect Cultivated Plants from Weeds and Pathogens



T. G. Volova, S. V. Prudnikova, N. O. Zhila, N. G. Menzyanova, E. G. Kiselev,
E. I. Shishatskaaya, and S. Thomas

Abstract The present chapter is a synthesis of the authors' data on the design and use of extended-release formulations of herbicides and fungicides embedded in a degradable matrix of polyhydroxyalkanoates (PHA). The structure and physico-chemical properties of the experimental formulations and the kinetics of their degradation in soil and pesticide release have been reported. The favorable effects of the application of the experimental pesticide formulations in laboratory soil ecosystems in wheat plant communities infected with *Fusarium* plant pathogen and weeds have been described.

Keywords Slow-release formulations · Poly-3-hydroxybutyrate · Antifungal activity · Herbicidal effect · Controlled release · Physiological effects

1 Introduction

Increased accumulation of toxic and unrecyclable waste products caused by uncontrolled use of chemicals is one of the main global environmental problems. A way to meet this challenge is to expand the use of tools and methods of biotechnology, which may help to protect beneficial biota and enhance productivity in agriculture

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as well as reduce toxic impacts of chemicals on agroecosystems and the whole biosphere (Gavrilescu et al. 2015). Intensive farming involves the use of enormous amounts of various chemicals to control weeds, pests, and pathogens of crops. However, most of these substances are accumulated in biological objects, contaminate soil and water environments, harm living organisms, and upset the balance in natural ecosystems (Carvalho 2017).

One of the new directions aimed at reducing the risk of uncontrolled spread and accumulation of pesticides in the environment is the development and use of pesticides with a controlled release of the active substance embedded in a biodegradable matrix or covered by biodegradable coating. Nanotechnology is currently an important tool for increasing agricultural productivity. Nanotechnology-based systems perform an active compound sustained release, keeping between minimal concentration and maximum safe concentration. The nanotechnology-based systems reduce the amount of active compound required for biological response, also reducing environmental contamination risks, energy consumption, and labor costs (Oliveira et al. 2018, 2019).

An important component of the creation of such formulations is the availability of suitable materials with the following properties (Yusoff et al. 2016; Sarkar et al. 2018):

- ability to fit into the environment and global biosphere cycles, i.e. degradability;
- safety for living organisms and the environment;
- prolonged (weeks and months) presence in the environment and controlled degradation, during which non-toxic products are formed;
- chemical compatibility with fertilizers and pesticides;
- processability by generally accessible methods, which are also compatible with technologies for the production of fertilizers and pesticides.

Encapsulation of pesticides is a relatively new approach, although the first papers were published in the 1990s (Greene et al. 1992). Interest in such research is increasing every year. The authors of those studies noted the following advantages of using pesticide controlled-delivery systems:

- prolonged action due to continuous release of pesticides at a level sufficient for effective function over a long period;
- fewer treatments due to prolonged action after a single application;
- shorter time needed to apply such pesticides;
- lower contamination of the environment;
- longer activity of pesticides unstable in the aqueous medium;
- conversion of the liquid pesticide into the solid formulation, which simplifies shipping and decreases flammability of the formulation;
- lower toxicity to biota due to the reduction of pesticide mobility in soil and, therefore, lower accumulation in the food chain.

The key ingredient for the construction of slow-release formulations is the availability of the appropriate biodegradable carrier. Thus, it is important to find and

investigate materials with the necessary properties. The materials extensively studied as matrices for embedding agrochemicals are synthetic nondegradable polymers (polystyrene, polyacrylamide, polyethylene acrylate, polyamide, polyurethane, polycyanoacrylate) (Sarkar et al. 2018). One of the new research areas is the use of new pesticides formulations with controlled and targeted release of pesticide encapsulated in biodegradable polymer matrix (Grillo et al. 2014; Roy et al. 2014). In the environment, the polymer matrix undergoes degradation by soil microorganisms and there is gradual pesticide release into the environment (Ong and Sudesh 2016). The use of such products will help to reduce the amount of pesticides used and ensure the controlled delivery of pesticides during the whole growing season of the plant, preventing sharp releases into the environment that occur when plants are treated with free pesticides. These formulations can only be constructed if materials with the following properties are readily available.

Achievements in science and technology determine a wider use of products synthesized in biotechnological processes. Production of environmentally friendly materials possessing new useful properties remains one of the main problems today. The diversity of polymers with widely varying stereo-configuration and molecular weight and the feasibility of producing various composites with different materials create the basis for obtaining a wide range of new materials with valuable properties. Recently, there has been growing interest in biopolymers (polymers of biological origin). There are two major kinds of biopolymers: polymers synthesized by biological systems (microorganisms) and chemically synthesized polymers based on biological feedstocks (amino acids, sugars, fats) (Chanprateep 2010).

2 Polyhydroxyalkanoates as a Basis for Pesticide Deposition

Among the biodegradable polymers that have already been developed or are being developed now for various applications, including medical ones, there are aliphatic polyesters, polyurethanes, polyamides, polylactides, polyglycolactides, silicon, polyethylene terephthalate, etc. These polymers are promising materials for fabricating biomedical devices, controlled drug delivery systems, degradable packaging for food and drinks, products for agriculture and public utilities (Lobo et al. 2011; Heng et al. 2017; Keskin et al. 2017).

Today, polyesters of monocarbon acids, polylactides (PLA) and polyglycolides (PGA), are the most widely used biodegradable polymers. The second most popular type of biodegradable polymers is polyhydroxyalkanoates (PHAs)—polymers of hydroxy-derived alkanolic acids. PHAs have lots of attractive properties including biodegradability and biocompatibility that make them promising materials for various applications, including biomedical ones (Sudesh and Hideki 2010; Volova et al. 2013, 2017b; Singh et al. 2012). PHAs have significant advantages in comparison with other biomaterials (Chen 2010):

- the high biocompatibility of PHAs, polyhydroxybutyrate in particular, is accounted for by the fact that the monomers constituting this polymer—hydroxybutyric acid—are natural metabolites of body cells and tissues;
- PHAs undergo true biological degradation, which occurs via the cellular and the humoral pathways; the resulting monomers of hydroxybutyric acid do not cause abrupt acidification of tissues and, therefore, do not give rise to any pronounced inflammatory reaction;
- PHA bioresorption rates are much lower than those of polylactides and polyglycolides; PHA-based implants can function *in vivo* for 2–3 years, depending on their form and implantation site; moreover, PHA degradation can be controlled;
- PHAs are produced by direct fermentation; no multistage technology is needed (monomer synthesis, polymerization, addition of plasticizers and modifying components);
- PHAs can be synthesized on such feedstocks as sugars, organic acids, alcohols, mixtures of CO₂ and H₂, products of plant biomass hydrolysis, industrial wastes of sugar and palm oil production, hydrogen-containing products of processing of brown coals and hydrolysis lignin;
- PHAs constitute a family of polymers of various chemical structures, consisting of monomers containing 4–12 and more carbon units, including high-crystallinity thermoplastic materials and rubber-like elastomers;
- PHA properties (crystallinity, mechanical strength, temperature characteristics, and biodegradation rates) can be controlled by varying the composition of the culture medium and tailoring the chemical structure of the polymer;
- PHAs can be processed from various phase states (powder, solution, gel, melt) using conventional techniques.

PHAs are very promising polymers as, being thermoplastic, like polypropylene and polyethylene, they also have antioxidant and optical properties as well as piezoelectricity. PHAs are highly biocompatible and can be biodegraded in biological media. In addition to poly(3-hydroxybutyrate) (P(3HB)), there are various PHA copolymers, which, depending on their monomeric composition, have different basic properties (degree of crystallinity, melting point, plasticity, mechanical strength, biodegradation rate, etc.). The properties of PHA polymers provide wide prospects for applications in various fields (public and agriculture, medicine and pharmacology, electronics, etc.).

PHAs are used to manufacture agricultural devices. These are films for greenhouses, packages for fertilizers and vegetables, pots, nets, ropes, etc. A new and environmentally important PHA application may be delivery of pesticides and fertilizers. Researchers of the Siberian Federal University and the Institute of Biophysics SB RAS were the first to prove that PHA can be used as a degradable base providing controlled release of fungicides and herbicides during the growing season of plants (Volova et al. 2008); pre-emergence formulations have been developed. That provided a basis for the new important use of PHAs—construction of slow-release formulations, in which chemicals for crop protection would be embedded in the matrix of these degradable polymers.

The ability of polyhydroxyalkanoates to break down in biological media is one of their most valuable properties. PHAs are degraded to water and CO₂ or to methane and water under aerobic and anaerobic conditions, respectively. Biodegradation of PHAs in the environment is carried out by extracellular depolymerases of microorganisms. Depolymerases are characterized by different molecular organization and specificity to substrate.

The analysis of the available literature shows that rather few authors reported on integrated studies of various aspects of PHA degradation, which is a very complex process. Most of the studies were performed in the laboratory, and they mainly dealt with the mechanism of interaction between the PHA supramolecular structure and PHA-depolymerizing enzymes, the structure and molecular organization of various depolymerases and microorganisms secreting extracellular PHA depolymerases.

An important question is the pattern of polymer breakdown in the natural environment. Extensive pioneering research on PHA biodegradation behavior in natural soil ecosystems was performed at the Siberian Federal University and Institute of Biophysics SB RAS.

We studied the kinetics and laws of the degradation of PHA in natural ecosystems in various regions and received answers to key questions of the PHA biodegradation process:

- which microorganisms are the most effective PHA degraders;
- how do the PHA properties change during degradation;
- how do environmental conditions (temperature, salinity, oxygen availability, pH, etc.) affect this process;
- how the process of PHA degradation will be affected by weather and climate of different regions.

PHA degradation influenced the total counts of microorganisms and composition of soil microflora. The microbial community formed on the polymer surface and the soil microbial community were different in the composition and percentages of the species. By employing the clear zone technique, we, for the first time, showed that each of the PHA types studied had specific degraders. PHA degradation behavior was studied in different environments: Siberian soils under broadleaved and coniferous trees, tropical soils (in the environs of Hanoi and Nha Trang), seawater (the South China Sea), a brackish lake (Lake Shira), and freshwater recreational water bodies in Siberia. Those studies showed that degradation occurred at different rates depending on the polymer composition, shape of the specimen (film or 3D construct), climate and weather conditions, and microbial community composition. The time over which the polymer loses 50% of its mass may vary between 68.5 and 270 days in Siberian soils, between 16 and 380 days in tropical soils of Vietnam, between 73 and 324 days in the brackish lake (Shira), between 127 and 220 days in the seawater of the South China Sea, and between 17 and 65.9 days in freshwater lakes (Prudnikova and Volova 2012). (Reprinted by permission from Springer Nature Customer Service Center GmbH: Springer Nature, Microbial Ecology, Microbial degradation of polyhydroxyalkanoates with different chemical

compositions and their biodegradability, Volova TG, Prudnikova SV, Vinogradova ON, Syrvacheva DA, Shishatskaya EI, 2017).

The studies of PHA degradation in different soils showed that the following conditions affect the degradation of PHA: polymer composition, its geometry and the technique used to process it, weather conditions, the type of the ecosystem and its microbial component in particular, as the factor determining the mechanism of PHA biodegradation: preferential attack of the amorphous regions of the polymer or equal degradation of both crystalline and amorphous phases. PHA degrading microorganisms that dominate microbial populations in some soil ecosystems have been isolated and identified.

The data on the degradation of PHA under natural conditions are very important and they form the basis for the use of these polymers as a basis (matrix) for the deposit of pesticides in order to create long-term and targeted plant protection products.

3 Experimental Formulations of the Fungicide Tebuconazole and Their Efficacy

Fungicides are necessary for modern high-performance crop farming to protect crops from pests and diseases. The total crop loss in the world from pests is about 35%, and it is even higher in developing countries (48%). Approximately 1/3 of these losses are due to plant diseases caused by bacteria, fungi, and viruses, which reduce the quality of products and cause poisoning of animals and people. Mycotoxins, which are produced by some disease agents, pose a serious danger. One of the most common diseases of crops is fusarium infection, caused by a soil pathogenic fungus belonging to the genus *Fusarium*. The use of fungicides leads to a fusarium infection decrease and reduction of mycotoxin content in grain.

Triazoles are the largest group of fungicides that can be used for treating plants in the early stages of the disease development or for preventive treatment. One of the widely used triazoles nowadays is tebuconazole (TEB). TEB is a broad-spectrum systemic fungicide against crop diseases (fusarium infection, rust, rots, powdery mildew, and others), some diseases of grapes, soya bean, rapeseed, sunflower, and vegetables. TEB inhibits the process of ergosterol biosynthesis in the cell membranes of plant pathogenic fungi, resulting in the disruption of cell membranes, causing the death of pathogen. Studies addressing the use of PHA as a matrix for embedding pesticides are few. The use of the P(3HB/3 HV) copolymer for production of microspheres loaded with the ametrine and atrazine herbicides was shown by Lobo et al. 2011; Grillo et al. 2011. Suave et al. (2010) reported encapsulation of the malathion insecticide in microspheres from P(3HB) blended with polycaprolactone. There is no information in the available literature on the use of PHA as a matrix for embedding fungicides. Commercial formulations of TEB, represented by suspen-

sions or emulsions used for spraying plants, are used widely. The fungicide is released from these formulations too quickly, which affects its effectiveness, and the fungicide has to be applied again. Thus, in order to increase the effectiveness of TEB and reduce its harmful effects on the environment, new formulations with controlled release of TEB are needed.

To construct environmentally friendly forms of TEB, biodegradable polymer P(3HB) was used as a matrix. The procedure for creating slow-release formulations of TEB in the form of films and pellets was described by Volova et al. (2016a). P3HB/TEB formulations were studied using X-ray structure analysis, differential scanning calorimetry, and Fourier transform infrared spectroscopy. Another study described TEB release from P3HB/TEB formulations into sterile distilled water and soil (Volova et al. 2017a). The fungicidal effect of P3HB/TEB formulations against the plant pathogen *Fusarium verticillioides* (formerly *Fusarium moniliforme*) was compared with that of Raxil Ultra (commercial formulation) (Volova et al. 2017a). In the first 2–4 weeks after the application, there was a noticeable fungicidal effect of the P3HB/TEB formulations, and it lasted for 8 weeks. In addition, no significant impact of experimental formulations on the soil aboriginal microflora was revealed. TEB release was found to depend on the TEB loading and the geometry of the formulation constructed, and TEB release in the soil occurred gradually, as P(3HB) was degraded.

Particular attention was paid to the study of potential for designing embedded target-delivery formulations of polymeric fungicides by nanotechnology-based systems (Shershneva et al. 2019).

The surface morphology of the P(3HB)/TEB microparticles was studied using scanning electron microscopy (SEM) (Fig. 1a, b). SEM analysis showed the presence of large undissolved crystals of TEB on the surface of microparticles. That was probably caused by the high concentration of TEB, which did not dissolve completely because of the presence of high-molecular-weight chains of P(3HB) in the solution. With the TEB increase in microparticles from 10 to 50%, the amount of TEB crystals on the surface of microparticles increased too. Apparently, the increase in encapsulation efficiency resulted from the high adsorption of TEB crystals on the surface of microparticles with the initial 50% TEB concentration in the solution (Table 1).

Moreover, a direct relationship between the TEB loading and the average diameter of microparticles was noted: with TEB loading increased from 10 to 50%, the average diameter of microparticles increased from 41.3 to 71.7 μm (Table 1). By contrast, as the TEB loading was increased, the yield of microparticles, regardless of the polymer initial mass, decreased. As for zeta potential, no effect of the TEB loading on the zeta potential was detected (Table 1).

Evaluation of the size distributions of microparticles showed that, as a percentage, particles with a diameter of about 50 μm prevailed over all concentrations of TEB loading. The proportion of the smallest particles with a diameter of 25 μm

Fig. 1 SEM images of P(3HB)/TEB microparticles before (a, b) and after (c) exposure to the soil; bars—200 μm (a, c) and 2 μm (b)

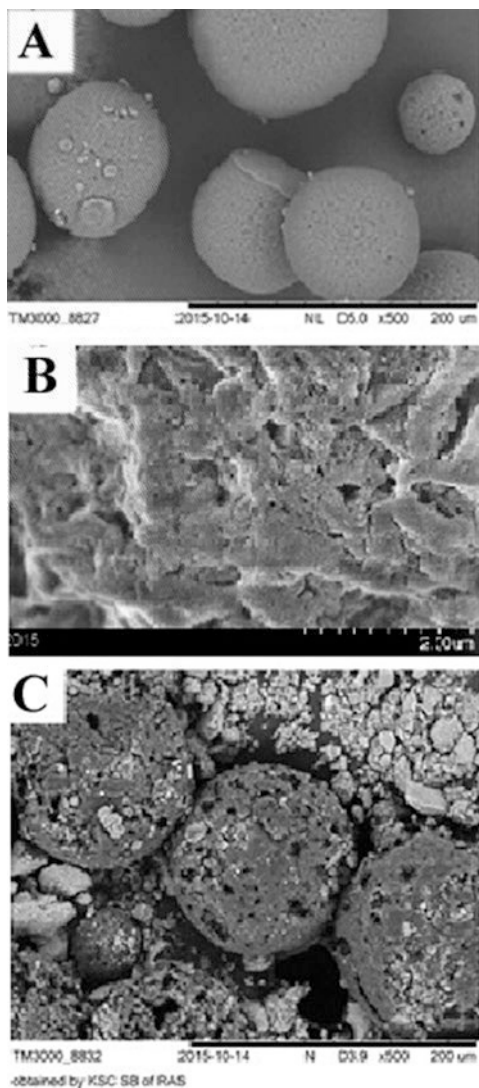


Table 1 Characteristics of P(3HB)/TEB microparticles with different amounts of TEB

Sample	Encapsulation efficiency (%)	Yield of particles (%)	Average diameter (μm)	Zeta potential (mV)
P(3HB)/TEB-10	59	70.9	41.3	-35.7 ± 2.0
P(3HB)/TEB-25	65	63.0	63.2	-32.6 ± 0.9
P(3HB)/TEB-50	86	58.5	71.7	-35.3 ± 2.1

increased while the TEB load was reduced to 10%. Conversely, with an increase in TEB loading to 50%, the proportion of large microparticles with a diameter of 125 μm and more increased significantly. Thus, the average diameter of the microparticles increased with the load of TEB from 41.3 to 71.7 μm . The emulsion technique makes it possible to obtain nanoscale microparticles that can penetrate plant tissue and are suitable for post-harvest processing and protection from damage to the aerial parts of plants (Ding et al. 2011; Qian et al. 2013). Larger microparticles obtained in our research can be used for pre-sowing treatment of seeds or pre-emergence introduction of fungicides into the soil together with the seeds.

TEB release from P(3HB)/TEB microparticles into sterile distilled water and soil was studied. TEB release from microparticles in distilled water during 60 days is indicated in Fig. 2. TEB release from microparticles with the TEB loading of 25 and 50% was similar. A possible reason for this may be low water solubility of TEB. This is probably associated with the low water solubility of TEB, and therefore, when the concentration of TEB in water reached its highest possible level, the rate of TEB release from the microparticles with 25 and 50% of TEB loading slowed down. TEB crystals were found on the surface of the 50% loaded microparticles at the end of the experiment, suggesting partial TEB release from microparticles, and thus, prolonged release of TEB was achieved. By the end of the experiment, TEB release from microparticles with 10, 25, and 50% of TEB was 43, 38, and 25%, respectively. Thus, the reason for slow TEB release from microparticles is apparently low water solubility of TEB. These results suggest that release of the fungicide can be regulated by changing TEB content in microparticles.

The exposure of TEB-loaded microparticles in soil microcosms led to the degradation of the polymer matrix of microparticles and a more intensive TEB release into the soil compared with the release to water. Obvious changes in the morphology of microparticles after 21 days of exposure can be seen on SEM images: partial destruction, the appearance of surface erosion, hollows, and cavities (Fig. 1c). After

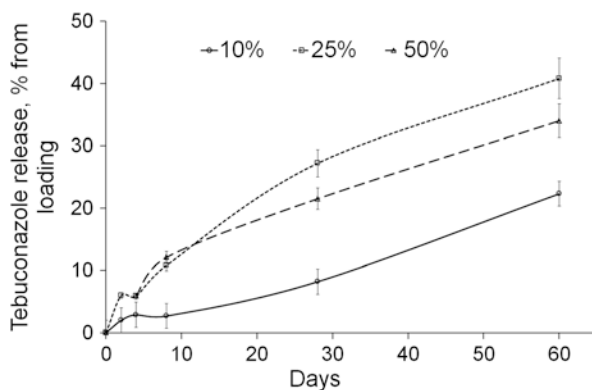


Fig. 2 Release kinetics of TEB from P(3HB)/TEB microparticles with 10, 25, and 50% of TEB loadings

35 days, the microparticles degraded by 80% and looked like small fragments of irregular shape with through holes and tunnels.

Antifungal activity of P(3HB)/TEB formulations with the TEB loading of 25% was studied in experiments with pathogenic fungi *Fusarium verticillioides*. This species of *Fusarium* genus is dangerous for people, because it not only damages the grain yield, but also produces mycotoxin (fumonisin), causes mycoses in immunocompromised people and has oncogenic potential (Voss et al. 2002).

The experiment was performed in vitro by growing *Fusarium verticillioides* on malt-extract agar in Petri dishes. As a positive control, 200 μL of commercial fungicide Raxil Ultra (Bayer AG, Germany) containing 120 mg L^{-1} of TEB was added to an agar-well. This dose was consistent with the load of TEB in the formulations. The experiment showed that the growing zone of the *F. verticillioides* decreased by two to three times under the influence of commercial fungicide and experimental TEB formulations. No significant differences were observed between the diameters of colonies in the positive control group and in the group of P(3HB)/TEB microparticles. Thus, the antifungal activity of P(3HB)/microparticles is comparable with the antifungal activity of commercial TEB, and it follows that experimental formulations of embedded TEB hold promise for constructing long-term formulations of TEB.

The efficacy of P(3HB)/TEB formulations was investigated in rhizosphere soil of wheat plants infected by plant pathogen *F. verticillioides* (Volova et al. 2018). TEB was embedded in degradable microbial polymer, P(3HB), designed as microgranules and films. Germination test of wheat seeds on the nutrient medium showed the presence of phytopathogenic fungi *Fusarium*, *Bipolaris*, and *Alternaria*. The total contamination of wheat seeds reached 9.5%, and 5.6% of which were *Fusarium* species. Thus, internal seed infection leads to the development of seedling disease in the early stages, inhibits the growth of plants, and reduces their productivity.

The developed experimental formulations of P(3HB)/TEB were placed into the soil simultaneously with the sowing of wheat seeds, and their fungicidal activity was compared with the effect of traditional used preparations: pre-sowing treatment of seed or soil treatment with Raxil Ultra. In the experiment with the initially infected seeds and low level of background fusarium infection ($3.1 \times 10^3 \text{ CFU g}^{-1}$), the experimental P(3HB)/TEB formulations did not differ in root pathogens suppression from commercial fungicide Raxil Ultra. However, in simulated conditions of high infectious load of the soil with pathogenic fungi *F. verticillioides*, the fungicidal activity of the P(3HB)/TEB formulations exceeded the effectiveness of the commercial fungicide. Before the experiment, the number of introduced *Fusarium* fungi reached one million per/g soil (including *F. verticillioides* and minor species), while the number of saprotrophic fungi was $25.2 \times 10^3 \text{ CFU g}^{-1}$. Due to competitive relationships in microbiocenosis, the total counts of *Fusarium* genus decreased to $21.2 \times 10^3 \text{ CFU g}^{-1}$ in the negative control after 30 days. For the same reason the total counts of saprotrophic fungi have been reduced to $4.9 \times 10^3 \text{ CFU g}^{-1}$. The counts of saprotrophic and phytopathogenic fungi were 9.2×10^3 and

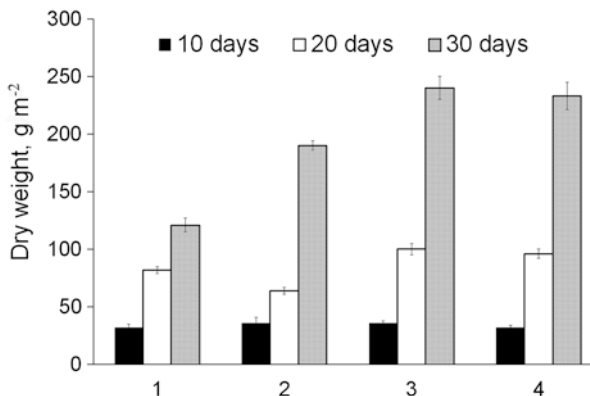
8.4×10^3 CFU g^{-1} , respectively, when Raxil Ultra was used. Therefore, fungicidal activity of P(3HB)/TEB formulations in soil with a high concentration of *F. verticillioides* was higher than when using commercial fungicide.

The infection of seeds and plants in contaminated soil by plant pathogens cause significant damage of roots. Nevertheless, even in case with naturally infected soil, *Fusarium* infection was also found in the first 10 days in all groups of plants, including the groups with TEB treated soil. This happened due to the fact that the seeds were infected with phytopathogenic microscopic fungi, and the infection had already appeared at an early stage of the seedlings. Then, the infection of plant roots not treated with fungicide increased. From 10 to 30 days, the number of plants infected with root rot increased (from 17 to 30% of the total number of tested plants). It was shown that infection caused by fungi of the genus *Fusarium* made its main contribution to the etiology of root rot (50–80% of all infections).

So, TEB is an effective fungicide used to protect different cereal crops. However, triazole fungicides, including TEB, are phytotoxic. Fungicides of triazole group suppress biosynthesis of ergosterol in cell membranes of pathogens and cause their death. Thus, crops infected by *Fusarium* and treated with triazole fungicides are affected by two negative factors: phytopathogens and pesticides. To identify the mechanism of the damaging effect of these factors, culture of *Triticum aestivum* infected with phytopathogens (*Alternaria*, *Fusarium*) and treated with triazole fungicides (tebuconazole) was used. The morphology of root apexes with population of border cells and the composition of exometabolites (proline, carbonylated proteins, and malonic dialdehyde) were analyzed (Shishatskaya et al. 2018). Proline (an integral indicator of the activity of antioxidant root systems), carbonylated proteins (CP), and malonic dialdehyde (MDA) are the indicators of the level of oxidative modification of proteins and activity of membrane lipids peroxidation.

At Day 10, the contents of MDA, CP, and proline in roots of the control wheat plants (group 1, without TEB application) did not differ significantly from their contents in plants roots of groups 2 (the treatment with Raxil Ultra applied to the soil) and 3 (the treatment with seeds pretreated with Raxil Ultra). At Day 20, the amount of MDA and proline in roots of group 1 increased considerably (by a factor of 8.5 and by a factor of 19) compared to Day 10, while CP decreased slightly (by a factor of 1.8). At Day 30, proline content in the roots of group 1 decreased dramatically, while MDA and CP contents did not change significantly. In group 2, contents of MDA, CP, and proline in the roots did not differ significantly from the control, suggesting that phytotoxic effects of TEB were softened as soil contamination with phytopathogens decreased. However, in group 3, contents of proline, MDA, and CP in the roots were higher than in group 1 by a factor of 2.2, 2.0, and 1.7, respectively. That was indicative of the activation of phytotoxic stress and free radical processes, as the effect of TEB used to pretreat the seeds before sowing must have been exhausted by Day 30. This study showed that the effect of TEB on redox homeostasis in wheat roots varied depending on the growth stage of plant and was considerably different in ecosystems with plants and soil infected by *Fusarium*

Fig. 3 The effect of TEB delivery mode on the increase in wheat aboveground biomass: 1—negative control, 2—positive control (Raxil applied to soil), 3—P(3HB)/TEB microparticles (10% TEB), 4—P(3HB)/TEB microparticles (25% TEB)



phytopathogens. At Day 20 of plant growth, during the tillering stage, TEB produced the strongest phytotoxic effect on wheat plants.

The results of evaluating the productivity of wheat communities in experiment with high degree of soil infection and root damage caused by rot are shown in Fig. 3. At Day 10, the aboveground biomass of wheat plants was comparable in the negative and positive control groups and in the treatment groups (P(3HB)/TEB microparticles). At Day 30, in the group with Raxil, the aboveground biomass reached 190 g m⁻², while in the treatment groups it was higher (230–240 g m⁻²).

The fungicidal activity of the experimental slow-release formulations of TEB embedded in the matrix of degradable P(3HB) against fusarium infection of wheat was comparable to that of TEB in commercial formulation Raxil in early stages (Day 10). In the later stages, P(3HB)/TEB formulations more effectively suppressed the development of *Fusarium* in soil and inhibited the growth of plant root rot.

4 Experimental Formulations of Herbicides and Evaluation of Their Efficacy

[Weeds cause great damage to agriculture, and herbicides constitute the most extensively used group of pesticides (40–50%), their commercial varieties accounting for about 40% of all commercial pesticides. Weed control using herbicides is one of the major components of modern efficient agriculture. However, herbicides, as well as other pesticides, persist in the soil, posing a hazard to human health, leading to the emergence of herbicide-resistant weed species, threatening the stability of agroecosystems and leaving the ground almost permanently barren. Much research effort has been recently focused on constructing new formulations and investigating their behavior in the environment. The main purpose of such studies is to produce less toxic and more selective pesticides and reduce the rate of pesticide application.] (Reprinted by permission from Springer Nature Customer Service Center GmbH: Springer Nature, Environmental Science and Pollution Research,

Poly(3-hydroxybutyrate)/metribuzin formulations: characterization, controlled release properties, herbicidal activity, and effect on soil microorganisms, Volova T, Zhila N, Kiselev E, Prudnikova S, Vinogradova O, Nikolaeva E, Shumilova A, Shershneva A, Shishatskaya E, 2016).

Triazines are commonly used broad-spectrum selective herbicides, which do not persist for a very long time in soil. Metribuzin (MET) is a pre-emergence and post-emergence herbicide which is used to treat different crops and has high biological activity in various climate zones (Fedtke 1981). [MET has been used by many researchers as a herbicide for constructing slow-release formulations based on various synthetic and natural materials: polyvinylchloride, carboxymethyl cellulose (Kumar et al. 2010a), acrylamide (Sahoo et al. 2014), methacrylic acid combined with ethylene glycol and dimethacrylate (Zhang et al. 2009), sepiolite (Maqueda et al. 2008), alginate (Flores-Céspedes et al. 2013), phosphatidylcholine (Undabeytia et al. 2011), kraft lignin (Chowdhury 2014), lignin/polyethylene glycol blends (Fernández-Pérez et al. 2011, 2015), chitin, cellulose, starch (Fernández-Pérez et al. 2010; Rehab et al. 2002), bentonite, activated carbon (McCormick 1985), etc. Thus, by varying the shape of the carrier, the technique employed to construct it, and the material used, one can influence MET release kinetics and design-controlled delivery systems for this herbicide.] (Reprinted by permission from Springer Nature Customer Service Center GmbH: Springer Nature, Environmental Science and Pollution Research, Poly(3-hydroxybutyrate)/metribuzin formulations: characterization, controlled release properties, herbicidal activity, and effect on soil microorganisms, Volova T, Zhila N, Kiselev E, Prudnikova S, Vinogradova O, Nikolaeva E, Shumilova A, Shershneva A, Shishatskaya E, 2016).

Degradable polymers of various origins are being tested as materials for constructing pesticide carriers. A review of current literature shows that polymers based on derivatives of carbonic acids have attracted the attention of many researchers. Special attention is given to polyhydroxyalkanoates (PHAs)—microbial polymers having many useful properties. [Production of polyhydroxyalkanoates (PHAs) is a rapidly developing branch of the industry of degradable bioplastics, and they are regarded as candidates to eventually replace synthetic polymers (Chen 2010; Ienczak et al. 2013; Kaur and Roy 2015; Volova et al. 2013).] (Reprinted by permission from Springer Nature Customer Service Center GmbH: Springer Nature, Environmental Science and Pollution Research, Poly(3-hydroxybutyrate)/metribuzin formulations: characterization, controlled release properties, herbicidal activity, and effect on soil microorganisms, Volova T, Zhila N, Kiselev E, Prudnikova S, Vinogradova O, Nikolaeva E, Shumilova A, Shershneva A, Shishatskaya E, 2016).

The purpose of this study was to investigate the herbicidal activity of MET embedded in the polymer matrix based on degradable poly(3-hydroxybutyrate) [P(3HB)] by exposing in laboratory soil ecosystems with higher plants. For the first time construction and investigation of slow-release MET formulations of different geometries with metribuzin embedded in the P(3HB) were described in Volova et al. (2016b). The P(3HB)/MET mixtures (powders, solutions, and emulsions) were used to construct MET-loaded pellets, films, granules, and microparticles and tested. Using X-ray, DSC, and FTIR methods the absence of chemical bonds between the