Degradation Processes of Pesticides Used in Potato Cultivations

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1 Introduction

Potato comes from the Andes in South America, where it was called *batata* in indigenous language. In the sixteenth century Spanish conquistadors brought it to Europe. They called the tubers *patatas* which evolved into the English word *potato*. During the next centuries, the consumption of this vegetable has been steadily increasing. In the world, potato is the fourth most commonly grown crop, after rice, wheat and maize (Barceloux 2008; Chang et al. 2012; Chiipanthenga et al. 2012).

High fiber, carbohydrates, as well as water-soluble vitamin concentration and low-fat content make potato tuber, the edible part of potato, a valuable comestible (Lazzarini et al. 2005; Webb and Smith 2011).

The chemical composition of a tuber is presented in Fig. 1 (Source: The potato: Tuber).

The green parts of potato plant (especially sprouts, stems and green skin) contain toxic glycoalkaloids: α-solanine and α-chaconine. The content of glycoalkaloids varies considerably between different cultivars depending on the strain and postharvest conditions (light, mechanical injury, temperature storage). In vitro studies indicate that both α-solanine and α-chaconine are reversible inhibitors of human plasma cholinesterase. Clinical features of α-solanine poisoning include gastrointestinal and neurologic symptoms, particularly vomiting, headache, and flush (Barceloux 2008).

Numerous potato cultivars are susceptible to viral diseases, and are frequently infected by various bacteria and fungi. They are also hosts for various insects. Moreover, during the rather long vegetative period weeds disturb the growth of the potatoes (Kryczyński 2010).

Therefore, to increase the efficiency of the farm production and the quality of this crop, the pesticides are used worldwide.

Some examples of potato diseases caused by different pathogens were listed in Table 1.

Potato cultivation is attacked by different pathogens, such as viruses, bacteria, fungi, and is destroyed by weeds and insects. It is necessary to use agrochemicals, which are a mixture of pesticides characterized by different chemical properties.

Fig. 1 The chemical composition of potato tuber

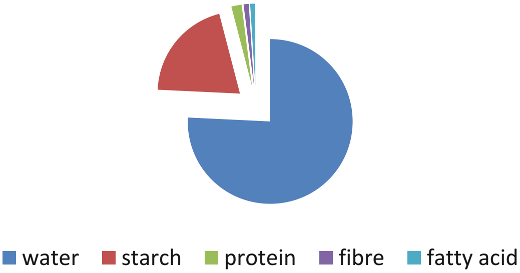


Table 1 Potato diseases (Sources: Hooker 1981; International year of potato 2008; University of Kentucky, College of Agriculture, Food and Environment)

Disease	Origin	Characteristic
Potato blackleg	Bacterial	Causes tubers to rot in the ground and in storage
Brown rot		Wilting and yellowing of the foliage
Ring rot		Witling of leaves and stem, vascular ring of tuber and stem
Pink eye		Pink areas which turn brown and it may transform in cavities
Late blight	Fungal	Destroys leaves, stems and tubers
Powdery snab		Forming raised lesions
Wart		Developing of warty outgrowthing at the stem
Skin spot		Light brown lesions on roots and stems
Leak		Causes swollen of potato's tuber
Pink rot		Wilting of leaves
Powdery middle		Light stipples on stems (initially powdery white)
Septoria leaf spot		Lesions on leaves rounded oval rings
Potato tuber moth	Pest	The most damaging pest of planted and stored potatoes in warm, dry areas
Melon thrips		Losing of potato vigour
Colorado potato beetle		Destroying of leaves and stems of potatoes
Aphids		
Potato leafhopper		

It is also important to control pesticides degradation in plants, soil and water, because their derivatives can be more toxic and stable in environment than parent compounds. Therefore, this article is dedicated to the degradation processes of selected pesticides used in potato cultivation, their toxicity and influence on human.

2 Pesticides

Pesticides (from Latin *pestis*—pest, *ceadere*—to kill) are a group of chemical compounds characterized by high toxicity. According to the definition of the Polish Environmental Protection Agency, pesticides are substances or mixture of substances which can destroy undesirable forms of plants, animals, and microorganisms or inhibit growth of pests (Seńczuk 2005).

Already in the Antique pesticides were used as plant protection products, e.g. arsenic—to control insects on plants; in the Middle Ages—an insecticidal powder—pyrethrum, while in the eighteenth and nineteenth century tobacco infusion was used against aphids (Seńczuk 2005).

The first synthetic pesticide, potassium dinitroorthocrezolate, was introduced in 1892, but the discovery of pesticidal properties of DDT (dichlorodiphenyltrichloroethane) and its use during World War II marked the beginning of the development, synthesis and use of pesticides on a large scale (Sikorska and Wędzisz 2009).

Application of pesticides has advantages and disadvantages. The advantages include: an increase in the crop yield, reduction in the frequency of animal, bird and human epidemics, the persistence of industrial products, e.g. paper or textiles. Main disadvantages include: contamination of water reservoirs and soil as a result of the transfer by wind or rain, bioaccumulation and toxic effects on non-target organisms including humans (Seńczuk 2005).

Insecticides are a class of pesticides of both natural and synthetic origin that are used to destroy insects or disrupt their development processes. The most important classes of insecticides are: organophosphorous, carbamates, organochlorines, polychlorinated biphenyls, neonicotinoids and pyrethroids (Seńczuk 2005).

Organophosphorous are used mainly in agriculture as insecticides, although they show properties of fungicides and herbicides. They cause damage to the cuticle, gastrointestinal irritation or disrupt the functioning of the respiratory system of insects. They constitute a tri-phosphoric acids and esters triphosphates. They can be degraded by hydrolysis, but at $pH > 8$ rate of this type of decomposition is reduced. Products of hydrolysis are diesters which can be also decomposed to monoesters, even to phosphorus. They decompose easily inside or on the surface of the plants and in soil. Organophosphorous insecticides act directly or non-directly on cholinesterase, which degraded neurotransmitter, acetylcholine (Seńczuk 2005).

Carbamates are esters of N-alkyl carbamic acid. N-aryl derivatives are used as herbicides. Some of them possess also fungicidal properties. These compounds can be quickly degraded in soil but their products of degradation have low toxicity, similar to parent compounds. They can be easily hydrolyzed in alkaline environment (Seńczuk 2005).

Organochlorines include three chemical groups: dichlorodiphenyltrichloroethane (DDT) analogs, hexachlorobenzene (HCB) isomers and cyclodiene compounds. They have low water solubility, but they have high solubility in organic solvents, oils and fats. They are resistant to external factors such as humidity, pH, temperature and light. Initially, these properties were recognized as advantages, but their use and production must be limited due to the potential for bioaccumulation (Seńczuk 2005).

Polychlorinated biphenyls are chemical compounds, which consist of two benzene rings and chlorine atoms attached to biphenyl. They have a wide range of applications e.g. in addition to insecticides. However, their main use in lacquers or lubricating oils caused environment contamination and consequently condensation in the food chain, which was dangerous for humans and animals. Therefore, its production was banned by the United States Congress in 1979 and by the Stockholm Convention on Persistent Organic Pollutants in 2001 (Seńczuk 2005).

Neonicotinoids are nicotine related insecticides, since they originate from nicotine that was initially applied as a natural plant protection product. They possess either a nitromethylene, nitroimine or cyanoamine group, which provide the insecticidal activity. They act as agonists of insect synaptic and extrasynaptic nicotinic acetylcholine receptors. An essential enzyme in insect central nervous system—acetylcholinesterase—is responsible for breaking the neurotransmitter acetylcholine. Electro-physiological studies show that neonicotinoids, like thiamethoxam (TMX), act on nicotinic acetylcholine receptors by reducing the effect of acetylcholine, which affects nervous system of insects (Mickaël et al. 2012).

Pyrethroids are synthetic analogues of pyrethrins. These compounds have improved physical and chemical properties, and biological activity compared to their natural analogues (Lee et al. 2002).

Natural pyrethrins are esters consisting of an “acid” component, which has a cyclopropane core and “alcohol” component. They are natural toxins produced by the flower of *Chrysanthemum*. Already in Antique and in the Middle Ages the dried flowers were used as insecticides. In nineteenth century, in Europe appeared “Persian dust”, which was produced from dried flowers of *Chrysanthemum*. The powder of pyrethrum flower was also used as a plant protection product in Kenya, Tanzania and Ecuador (Elliott and Janes 1978; He et al. 2008).

The first synthetic pyrethroid was produced in twentieth century by alcohol substitutions in naturally occurring pyrethrins. Toxicity of pyrethroids is highly dependent on stereochemical structure (He et al. 2008; Koprucu and Aydm 2004).

Pyrethroids are the most lipophilic compounds among insecticides and they are characterized by high insecticidal and low mammal toxicity; they are biodegradable (Tabaeran and Narahashi 1998).

Classification of pyrethroids:

- Type I—insecticidal esters of chrysanthemic acid
- Type II—insecticidal esters of pyrethric acid

The pyrethroid insecticide affects the nervous system of insects. Type I pyrethroids (e.g., permethrin) only affect sodium channels. Type II compounds, such as lambda-cyhalothrin (LC) and deltamethrin (DM), have α-cyano group at the α-benzylic position (the α-carbon of the 3-phenoxybenzyl alcohol) and they also affect chloride and calcium channels, which are important for correction of nerve functions (He et al. 2008).

The different physiological effects are explained by the fact that the persistence of modified sodium currents by compounds of the first type lasts only tens or hundreds of milliseconds, while those of type II lasts for several seconds or longer (Elliott and Janes 1978).

Herbicides are a group of chemical compounds, both organic and inorganic, used for weed control. Organic herbicides are mainly derivatives of phenoxy acids, dinitrophenols, triazines and urea derivatives (Biziuk 2001; Seńczuk 2005).

Phenoxy acids include phenoxypropionic and phenoxybutyric derivatives. They are water-soluble. They destroy weeds by stimulating the endocrine system, what results in uncontrolled plants growth and their destruction. These compounds undergo photolysis, hydrolysis and biodegradation in environment. They do not pose a serious risk for human and animal health (Seńczuk 2005).

Dinitrophenols are compounds, which can be also used as insecticides, acaricides and ovicides. The mechanism of action is based on oxidative phosphorylation decoupling. They have low water solubilities and are characterized by high solubility in organic solvents. They are very toxic to mammals, beneficial insects and fish (Seńczuk 2005).

Triazines are highly toxic to mono- and dicotyledonous plants. They exhibit stability under soil conditions. They are photosynthesis inhibitors (photosystem II). The modes of their degradation are grouped into three types of reaction: dealkylation, oxidation, and dechlorination. Studies show, that chemical hydrolysis is the dominant degradation pathway for triazines (Seńczuk 2005).

Sulfonylureas became quickly accepted and popular because of low application doses, and favorable environmental and toxicological properties. They inhibit acetolactate synthase, an enzyme involved in the branched chain amino acid biosynthesis in plants, which inhibits weed cell growth. The soil half-life depends on soil pH and temperature. They decompose faster in warm and low pH soil conditions. Their water solubility is high and also depends on water pH. They can be degraded mainly via two pathways: hydrolysis and microbial activity. They do not pose a serious risk for environment and humans (Scrano et al. 1999; Nageswara Rao et al. 2012).

Fungicides are a large group of inorganic and organic compounds. They can act fungicidal (retain the growth and reproduction) or fungistatic (inhibition of the growth). They are used preventively. The most toxic to living organisms among all fungicides are inorganic mercury compounds, which, after long-term exposure, cause permanent damage of the nervous system, mental health and fatal poisoning, and therefore have been withdrawn from use (Seńczuk 2005).

Dithiocarbamates include three main groups: salts of dimethyl dithiocarbamates, ethylenebisdithiocarbamates and sulfides. They can be used in medicine to treat diseases caused by fungi and in agriculture both as fungicides as well as insecticides. Depending on their chemical structure, they can be characterized by low or high solubility in water. Heavy metals dithiocarbamates are characterized by low, but alkali metals are characterized by high solubility in water (Seńczuk 2005).

Phenylamides are selective fungicides used to control soilborne fungi *Pythium* and *Phytophtora* and foliar fungi that cause plant diseases. They belong to a group of systemic fungicides, which are taken up and distributed within plants and inhibit fungal growth by disrupting RNA synthesis. They are stable over a wide range of pH, temperature and light (Seńczuk 2005).

3 Degradation of Pesticides

Degradation of organic pollutants is a natural process of their decomposition in the environment. The degradation process is complete when the organic compound is decomposed to naturally occurring compounds; usually carbon dioxide and water (Dąbrowska et al. 2002).

Pesticides degradation in the environment is the result of biochemical processes, chemical reactions and photodegradation. Moreover, their decomposition may be a result of physical processes, e.g. evaporation or sublimation. Generally, the rate of polar pesticides degradation is higher, in comparison to nonpolar pesticides, due to the higher water solubility (Biziuk 2001). The main pesticides degradation processes, that occur in environment are: hydrolysis, photodegradation, and biodegradation.

Hydrolysis is a chemical process of chemical bond breaking in the presence of water, resulting in the conversion of the parent compound into its degradation product(s). Usually, it includes additional reactions: reduction, oxidation, and complexation. It may include also biodegradation and photodegradation processes, which occur in aqueous solutions (Katagi 2002).

Hydrolysis is also observed as one of the possible pathways of pesticides transformation in soil and living organisms. This process depends on pH and temperature, as well as metal ion presence, and dissolved organic matter (humic acids), which influence hydrolysis rate. Pesticides hydrolysis usually fits to first-order kinetics and the pesticide's disappearance rate is proportional to its initial concentration (Eq. 1) (Katagi 2002).

$$-\mathrm{d}[\mathrm{P}]/\mathrm{dt} = \mathrm{k}_{\mathrm{obs.}}[\mathrm{P}] \tag{1}$$

[P]—pesticide concentration
$\mathrm{k}_{\mathrm{obs}}$—observed hydrolysis rate concentration

Equation 1 allows calculating the pesticide half-life that does not depend on pesticide concentration, pH and temperature (Eq. 2).

$$\mathrm{T}_{1/2} = 0.693/\mathrm{k}_{\mathrm{obs.}} \tag{2}$$

$\mathrm{T}_{1/2}$—pesticide half-life

In the pH conditions of natural surface waters (5–8), most of pesticides are stable, e.g. pyrethroid insecticides or sulfonylurea herbicides. A higher rate of their degradation by hydrolysis is observed in alkaline and acidic conditions, respectively (Katagi 2002).

Photodegradation is a chemical process of organic compounds, e.g. pesticide, transformation, that occur under exposure to light. It occurs in the atmosphere, water and in upper soil layer. It can be classified into four groups: direct and indirect photodegradation, photosensitized degradation, photocatalyzed degradation (Burrows et al. 2002; Dąbrowska et al. 2002).

Direct photodegradation is based on photon absorption by molecules and they are transferred to the state of higher energy by homolysis, heterolysis or photolysis (Fig. 2). As a result of these processes chemical bonds are broken and parent compounds are transformed into various derivatives (Burrows et al. 2002; Dąbrowska et al. 2002).

Indirect photodegradation it is reaction with photo-oxidizing agents: OH-radicals, O_3 or NO_3, which naturally occur in the atmosphere. The mechanism

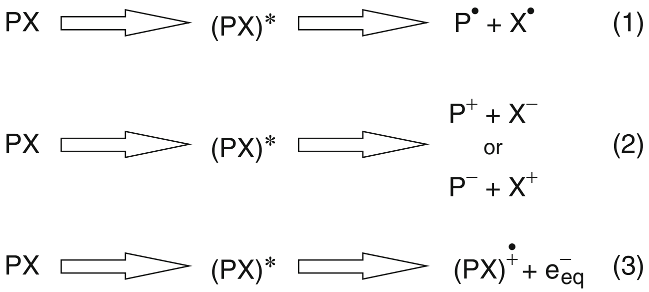


Fig. 2 Chemical reactions under direct photodegradation: (*1*) homolysis, (*2*) heterolysis, (*3*) photoionization

of this process consists of a few stages. Initially, a molecule absorbs the photon and chemical bond is broken. Then very reactive radical forms, e.g. OH are generated (Burrows et al. 2002; Dąbrowska et al. 2002; Chen and Liu 2008).

This indirect degradation process can be achieved by different ways:

- hydrogen peroxide addition

$$H_2O_2 + h\nu \rightarrow 2HO^{\bullet}$$

- ozone photolysis and singlet oxygen atoms generation and subsequently generation of $HO^{\bullet}$

$$O_3 + h\nu \rightarrow O_2 + O\left({}^1D\right)$$
$$O\left({}^1D\right) + H_2O \rightarrow 2HO^{\bullet}$$

- ozone photolysis and singlet oxygen atoms generation, which subsequently generate hydrogen peroxide

$$O_3 + H_2O + h\nu \rightarrow H_2O_2 + O_2$$

- Fe^{2+} oxidation by hydrogen peroxide

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO^{\bullet}$$
$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + HO^{\bullet} + H^+$$

- water hydrolysis

$$H_2O \rightarrow HO^{\bullet} + H^+ + e^-_{aq}$$

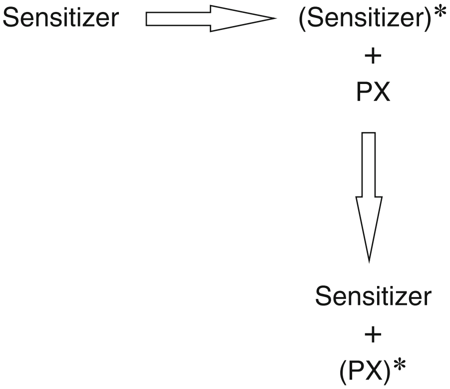


Fig. 3 Chemical reactions under photosensitized photodegradation

Photosensitized degradation is similar to direct photodegradation based on photon absorption by a molecule. The energy from its excited state (Sensitizer)* can be transferred to pesticide (PX) (see Fig. 3) (Burrows et al. 2002).

Subsequently, this excited compound can undergo homolysis, heterolysis and photolysis, even as a result of direct photodegradation. It also involves redox processes, e.g. the photo-Fenton reaction (an example is described in Sect. 5.1.2).

Photocatalytic degradation is a degradation process of pesticides, which involves catalysts and is conducted under light. It allows conducting continuous degradation process. Literature reports inform, that the following compounds are used as photocatalysts: Ag_2O/Ag_2CO_3 (Yu et al. 2014), Ag_3PO_4/TiO_2 (Yao et al. 2012), Fe_2O_3/TiO_2 (Palanisamy et al. 2013), TiO_2 (Guo et al. 2012; Liu et al. 2012; Kondrakow et al. 2014; Patel et al. 2014; Zheng et al. 2014), ZnO/CuO nanocomposite (Saravanan et al. 2013) and ZnO nanoparticles (Rahman et al. 2013).

Biodegradation is a multi-step process of biological decomposition of organic compounds involving microorganisms, in which their enzymes are used as catalysts. This degradation process can be defined as mineralization, when the organic compound is transformed into inorganic compound(s). Most of pesticides are transformed to organic compounds, which are characterized by different properties in comparison to the parent compounds. Microbial transformation includes: hydrolysis, hydroxylation, dehalogenation, ester or ether cleavage, deamination, nitro-reduction, methylation or demethylation (dealkylation) (Dąbrowska et al. 2002).

The following conditions are necessary to microbial activity:

- the microorganism must be present in environment containing the pesticide
- the pesticide must be accessible for the microorganism
- microorganism biomass should allow its proliferation

Biodegradation in the aquatic environment depends on the particulate matter presence, inorganic and organic nutrients, temperature, oxygen concentration, redox potential, bioavailability and microbial adaptation. In soil, it depends on soil temperature, soil moisture content, bacterial composition and activity, the properties and age of a pollutants and nutritive ingredients content (Dąbrowska et al. 2002).

4 Thiamethoxam

Thiamethoxam, 3-(2-chloro-1,3-thiazol-5-ylmethyl)-5-methyl-1,3,5-oxadiazinan-4-ylidene(nitro)amine, belongs to insecticides. It is a member of the second generation of neonicotinoids, in the thianicotinyl subclass (Maienfisch 2001, 2006).

TMX was first synthesized in 1991 and entered the market in 1998 by Syngenta Crop Protection. Like other neonicotinoids, it has been introduced to the market in order to replace organophosphates, a widely used group of insecticides. It is used as a soil, foliar and seed treatment agent for the control aphids, whiteflies and certain beetles (Maienfisch 2001; Hem et al. 2010).

The molecule of TMX contains two rings and five nitrogen atoms. N-nitroguanidine and the 2-chlorothiazole moieties are essential for biological activity of the compound. A replacement of this pharmacophore by other groups, e.g. $N(3)\text{-}C(N){=}NNO_2$, causes the loss of pesticidal activity of the compound. The pharmacophore “backbone”, a 1,3,5-oxadiazinane ring is characterized by stronger biological activity than any other heterocyclic ring, where instead of oxygen are $=N\text{-}CH_3$, $=S$, $\text{-}CH_2$. Introduction of a methyl group at N(5) leads to an increase in the insecticidal activity, but introduction other groups, e.g. hydrogen, ethyl, n-propyl or ester group, results in a complete loss of activity (Maienfisch 2001; Taillebois et al. 2014).

TMX is a moderately persistent compound in soil environment. The half-life in laboratory conditions is about 12 days, but in field conditions its degradation is slower, with a half-life of about 39 days. Degradation under field conditions is faster due to the presence of microorganisms and exposure to light. In aquatic environment its decomposition by light is moderately fast, but it is resistant to hydrolysis. Half-life of TMX in aqueous solution (laboratory conditions), at room temperature at pH 5 is more than 1 year, but at pH 7 is estimated at 200–300 days. It is more labile at pH 9 and with half-life a few days. In sediment systems it is degraded moderately fast, therefore does not cause contamination of water (Maienfisch 2001; Hem et al. 2010).

TMX is relatively non-toxic to birds, fish and mammals but it exhibits high toxicity to honeybees. Decrease of their population can negatively impact the natural crop pollination process (Mickaël et al. 2012).

Physical and chemical properties of TMX, including its half-lives in soil and water are listed in Table 2 (Source: The PPDB).

Table 2 Physical and chemical properties of pesticides, including their half lives in soil and water (Source: The PPDB)

Property		Thiamethoxam	Rimsulfuron	Metalaxyl	Lambda-cyhalothrin	Deltamethrin
Pesticide type		Insecticide	Herbicide	Fungicide	Insecticide	Insecticide
Substance group		Neonicotinoid	Sulfonylourea	Phenylamide	Pyrethroid	Pyrethroid
Substance origin		Synthetic	Synthetic	Synthetic	Synthetic	Synthetic
Chiral molecule		No	No	Yes	No	Yes
Chemical formula		$C_8H_{10}ClN_5O_3S$	$C_{14}H_{17}N_5O_7S_2$	$C_{15}H_{21}NO_4$	$C_{23}H_{19}ClF_3NO_3$	$C_{22}H_{19}Br_2NO_3$
Molecular mass (g mol^{-1})		291.71	431.44	279.33	449.85	505.2
Solubility in water at 20 °C (mg l^{-1})		4100	7300	8400	0.005	0.0002
Log P		−0.13	−1.46	1.65	5.5	4.6
Vapour pressure at 25 °C (mPa)		6.6×10^{-6}	8.9×10^{-4}	0.75	0.0002	0.0000124
Soil degradation (aerobic) (days)	DT50 (typical)	50	24.3	36	175	13
	DT50 (laboratory conditions at 20 °C)	121	24.3	36	175	26
	DT50 (field conditions)	39	10.8	38.7	26.9	21
Foliar DT50 (days)		–	3	30	5	3
Aqueous photolysis DT50 (days) at pH = 7		27	11.7	Stable	40	48
Aqueous hydrolysis DT50 (days) at 20 °C and pH = 7		Stable	7.2	106	Stable	Stable
Water sediments DT50 (days)		40	6	56	15.1	65
Water phase only DT50 (days)		3.6	4	56	0.24	17
Risk classification		Xn—harmful, N—dangerous for the environment	N—dangerous for the environment	Xn—harmful, N—dangerous for the environment	T+—very toxic, T—toxic, Xn—harmful, N—dangerous for the environment	T—toxic, N—dangerous for the environment

4.1 Abiotic Degradation of Thiamethoxam

4.1.1 Hydrolysis of Thiamethoxam

In details, the influence of pH on the persistence of four neonicotinoid insecticides: acetamiprid, thiacloprid, TMX and imidacloprid in water was described in Guzsvany et al. (2006). Among all investigated compounds TMX was the most stable in acidic conditions during 4 months. After 5 weeks of experiment conducted in water at pH = 7, in ^{1}H NMR (proton nuclear magnetic resonance) spectrum two signals were observed: one corresponded to TMX, and the second one belonged to TMX degradation product. The TMX hydrolysis was influenced by the pH of medium: the higher pH of medium, the hydrolysis was faster. The lowest persistence of TMX was observed at pH = 9 (Guzsvany et al. 2006; Maienfisch 2006). This conclusion was in agreement with the findings obtained by Zheng and Liu (1999) and Liquing and coworkers (2006). Moreover, IR (infrared spectroscopy) and GC-MS (gas chromatography–mass spectrometry) spectra analysis revealed, that there was only one main product of TMX hydrolysis. In comparison to parent compound, this derivative was stable in alkaline conditions.

According to above-mentioned studies, the main product of TMX hydrolysis was 3-(2-chloro-thiazolyl-5-ylmethyl)-5-methyl-4-oxooxadiazine. This pathway of TMX hydrolysis is presented in Fig. 4a.

The mechanism of TMX hydrolysis results from the character of its nitro group. This strong electron acceptor induces a small positive charge on the carbon of the cyano group in the oxidiazine ring. As a result it is easily attacked by hydroxyl anion (Liquing et al. 2006).

Another studies, which were conducted under laboratory conditions, on TMX degradation indicated that there is the second pathway of thiamethoxam hydrolysis.

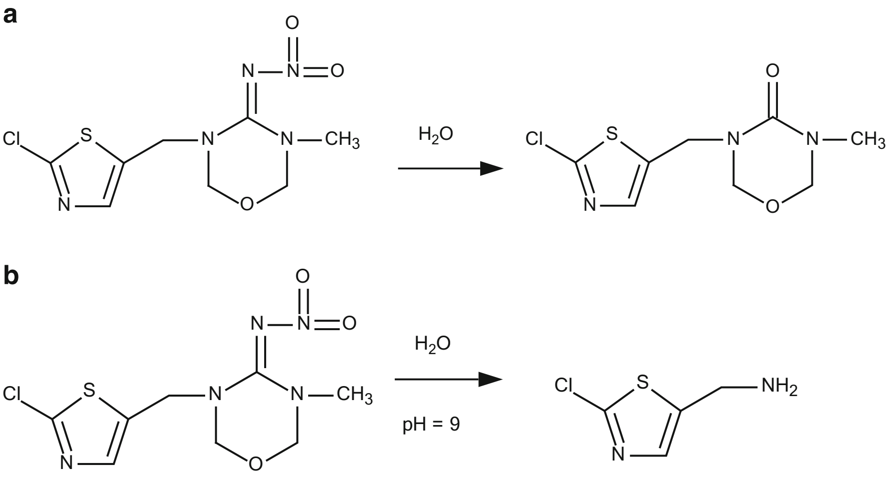


Fig. 4 Hydrolysis of TMX: (**a**) the first pathway (**b**) the second pathway

It leads to the opening of N-nitro-urea ring (at pH range in the range 5–9) and to the formation of 2-chloro-5-aminomethyl-thiazole, as presented in Fig. 4b (Maienfisch 2006).

Maienfisch (2006) observed, that harsh degradation conditions (concentrated HCl, 80 °C) gave clothianidin (that is also used as pesticide) as a TMX degradation product. It was an important observation for better understanding of its degradation process occurring in plants and insects, since these organisms converted TMX to clothianidin (Nauen et al. 2003).

4.1.2 Photodegradation of Thiamethoxam

Depending on the conditions, there are many pathways of TMX photodegradation (de Urzedo et al. 2007).

The first one, observed after exposure of TMX to artificial sunlight of photoperiods of 12 h over 12 days, is shown in Fig. 5.

Photodegradation of TMX was verified by de Urzedo and coworkers (2007) in aqueous solutions under UV radiation. Nucleophilic attack of H_2O on the nitro group in TMX (A), caused the formation of imine (B) and release of HNO_3. The conversion of compound B to the intermediate compound C occurred by nucleophilic substitution of the Cl atom by the OH group.

The same experiment showed that under these conditions TMX half-life was 10 min and this pesticide was completely degraded after 30 min. Simultaneously, the control experiment confirmed high stability of TMX in aqueous solution,

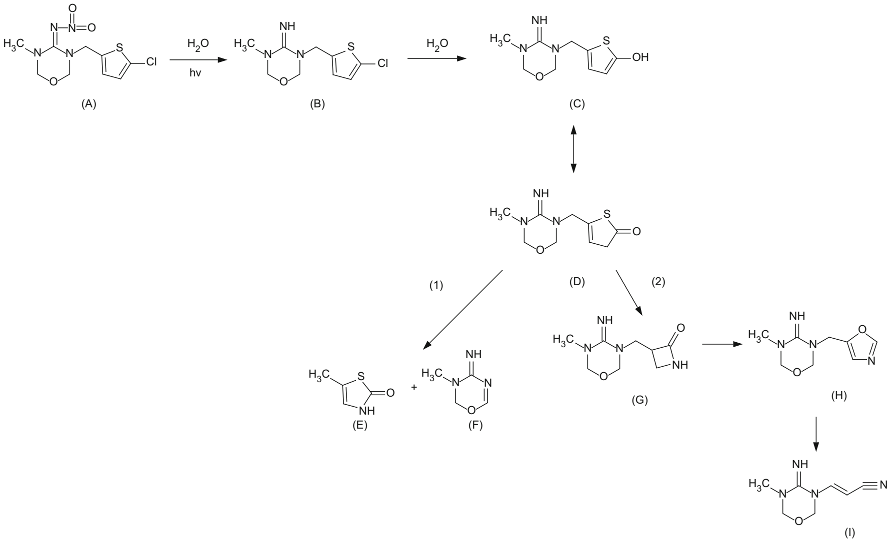


Fig. 5 The first pathway of TMX photodegradation

protected from UV light (de Urzedo et al. 2007). Mechanism of this reaction is similar to hydrolysis, which is presented in Sect. 4.1.1.

The product of the first pathway of TMX degradation, which is marked as compound D in Fig. 5, can be further degraded according to different pathways (Fig. 5).

Photolytic decomposition of metabolite D led to the formation of two degradation products: 5-methyl-2(3H)thiazolone (E) and compound F. The extrusion of the sulphur atom from compound D (second reaction) can generate azetidinone (G), which can be transformed to the oxazine (H). The final product of degradation (I) was formed by the hydrolysis of the imine group and the breakdown of the oxazol ring of compound H (third reaction) (de Urzedo et al. 2007). It is also possible, that photolytic degradation of TMX in aqueous medium may lead to formation of a carboxyl group instead of the imine (Schwartz et al. 2000).

As it is shown in Fig. 5, there are many pathways of TMX photodegradation, resulting from its complex structure—two rings and five nitrogen atoms. Moreover, the nitroguanidine group which is a chromophore, may decrease photolysis efficiency.

4.2 Biodegradation of Thiamethoxam

Metabolism of TMX by microorganisms in soil is the main pathway of its degradation. Because of TMX "magic nitro" group, which is responsible for its insecticidal activity and high selectivity to nAChR (nicotinic acetylcholine receptor), this moiety was thoroughly studied in biotransformation processes (Zhou et al. 2012).

According to literature reports, the following bacteria species are able to metabolize of TMX: *Pseudomonas sp.* strain 1G (Pandey et al. 2009), nicotine-degrading *Acinetobacter sp.* strain TW and *Sphingomonas sp.* strain TY (Wang et al. 2011), plant growth-promoting rhizobacteria *Bacillus subtilis* GB03, *Bacillus subtilis* FZB24, *Bacillus amyloliquefaciens* IN937a and *Bacillus pumilus* SE34 (Myresiotis et al. 2012), *Ensifer adhaerens* (Zhou et al. 2012), *Bacillus aeromonas* strain IMBL 4.1 and *Pseudomonas putida* strain IMBL 5.2 (Rana et al. 2015).

Proposed pathways of biotransformation of TMX by *Pseudomonas sp.* strain 1G are presented in Fig. 6 (Pandey et al. 2009).

As shown in Fig. 6, the "magic group" of TMX (A), is reduced to nitrosoguanidine =N-NO (B) and aminoguanidine –N-NH_2 metabolites (C). Subsequently these metabolites are converted to the nontoxic urea metabolite =O (E) and the more toxic desnitro/guanidine =NH metabolite (D) (Pandey et al. 2009). These degradation pathways were also found by Zhou et al. (2012) in mammals, mice and some plants (spinach and tomato).

Ensifer adhaerens is nitrogen-fixing microorganism, able to transform TMX (A) by the nitro-reduction of the nitroimino group to nitrosoimino (D) and urea (F). The major metabolic pathway of TMX in *Ensifer adhaerens* involved the transformation of its =N-NO_2 (N—nitroimino group) to =N-NO (N-nitrosoimino) and

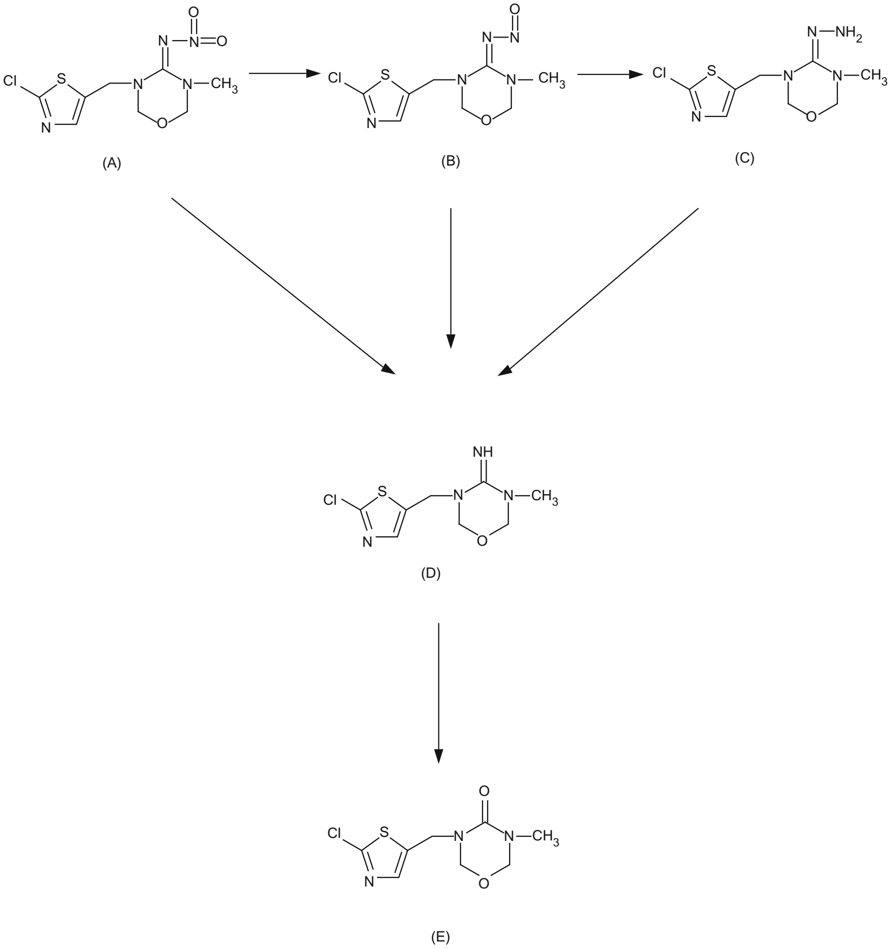


Fig. 6 Biotransformation of TMX by *Pseudomonas sp*. strain 1G

C=O (urea) metabolites. These compounds were also detected in mouse, insect and few plant (cotton, spinach and tomato) tissues exposed to TMX. This way of TMX degradation is presented in Fig. 7 (Zhou et al. 2012).

Moreover, in spinach, tomatoes, insects and mice organisms, desmethyl metabolite (B) is formed by N-desmethylation of TMX. Through the cleavage of oxidiazine ring clothianidin (C) is formed. This compound was also formed as a result of TMX hydrolysis (Zabar et al. 2012; Zhou et al. 2012).

Pathways of TMX degradation by microorganisms: *Pseudomonas sp* and *Ensifer adhaerens* were similar, as evidenced by the same intermediate degradation products (Figs. 6 and 7). Moreover, the final product of biodegradation was the same as a result of hydrolysis: 3-(-2-chlorothiazolyl-5-methyl-)-5-methy-4-oxadiazine. It suggested that degradation of TMX by these bacteria was based on hydrolysis (Pandey et al. 2009; Zabar et al. 2012; Zhou et al. 2012).

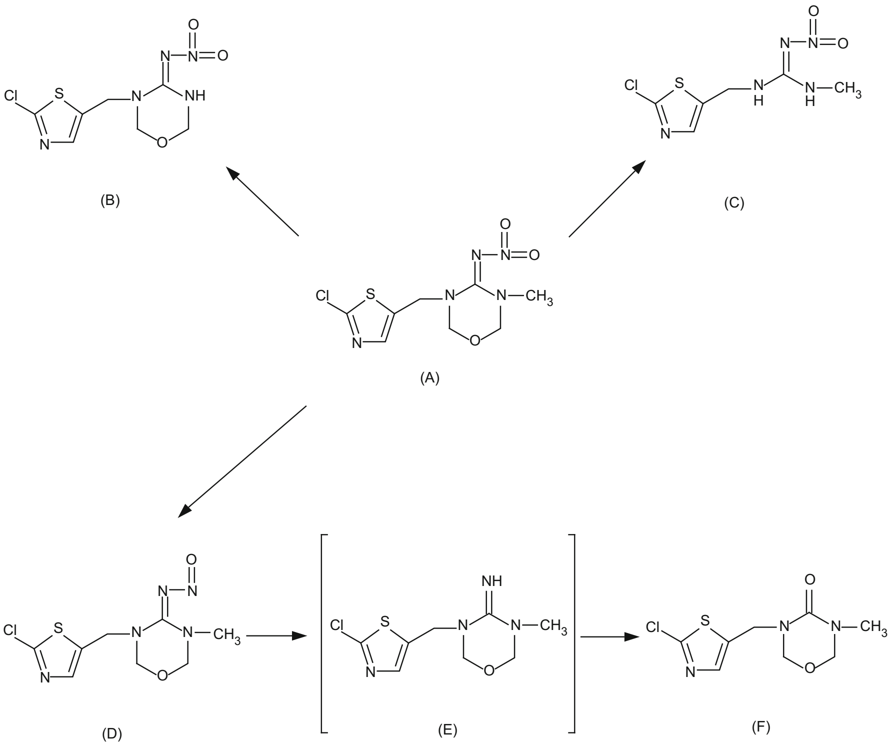


Fig. 7 Possible pathways of biodegradation of TMX by *Ensifer adhaerens*

4.3 Toxicity of Thiamethoxam

The influence of TMX and its degradation products on algae, zooplankton, bacteria, terrestrial plants, invertebrate species, and insect feeding birds was the objective of many studies, since TMX in one of the most spread insecticide in natural environment (over 25 % of total global insecticide applications (Bass et al. 2015)). Since its stability in the environment is, depending on conditions, in the range of 3.6–1000 days (Table 2; Bonmatin et al. 2015)) there is strong evidence that soils and waterways are contaminated with variable levels of TMX and its degradation products.

Šojić and coworkers (2012) investigated the ecotoxic effects of TMX and their UV-photolysis degradation intermediates (5-methyl-2(3H)thiazolone and imine) towards algae *Pseudokirchneriella subcapitata*, zooplankton *Daphnia magna* and bacteria *Vibrio fischeri*. The toxicity of TMX towards the algae culture was expressed by the normalized inhibition values of the solutions after 72 h incubation at 21 °C. The parent compound itself inhibited slightly the growth of *P. subcapitata*. However, at the end of the treatment (when the parent molecules were completely transformed) the toxicity of the solutions was higher than the normalized inhibition values of the initial solutions. The likely reason for this was the formation of degradation intermediates that were more toxic than the parent compound.

The toxicity of TMX towards *Daphnia magna* was expressed by the mortality rate of the zooplankton after 48 h of incubation at 21 °C. From the results it could be concluded that *Daphnia magna* was more sensitive to TMX degradation by-products and less sensitive to the parent compound than *P. subcapitata*. The mortality rate increased with the treatment time, suggesting the presence of toxic degradation products. Moreover, the investigations of mutagenicity and DNA breaking revealed that some very harmful degradation intermediates of TMX were produced in the photolytic processes (Šojić et al. 2012). The higher toxicity of TMX degradation products (the experiments were conducted on lettuce, *Lactuca sativa*) was confirmed by Laberge and Rollinson (2013).

Mir et al. (2013) conducted photocatalyzed degradation of TMX in aqueous suspension of TiO_2. Depending on the conditions of this reaction, a mixture of up to eight by-products was obtained. Most of them were different than naturally occurring TMX degradation products. Human erythrocytes as a model system under in vitro conditions were applied to access the toxicity of TMX and the mixture of its photocatalytic by-products.

On the basis of the obtained results, it was concluded that photocatalytic degradation of TMX led to reduction in toxicity implying that degradation intermediates were less toxic than the original substrate itself. Thus, the photocatalytic degradation of the organic compounds like TMX is a promising method for eliminating these compounds from water. However, as a result of the cleavage of oxidiazine cycle, clothianidin is formed, which is toxic for bees (*Apis mellifera*) (EFSA 2005; Zhou et al. 2012).

According to many studies (Beketov and Liess 2008; Blacquiere et al. 2012; Van den Brink et al. 2016), TMX as well as other neonicotinoids is very toxic to invertebrate, especially bees. Neonicotinoids concentrations present in pollen and nectar is the principal determinant of toxicity to individual bees or their colonies (Carreck and Ratnieks 2014; Bonmatin et al. 2015).

Since both TMX, classified as Xn—harmful, and N—dangerous for the environment (Table 2) as well as its degradation products exhibit negative effects on non-target organisms, there is a moratorium on neonicotinoid use as seed treatments, or as granules, on certain "bee attractive crops" such as maize, sunflower and oilseed rape in the European Union (EU) due to "high acute risks" to bees (Europa 2013; Balfour et al. 2015).

5 Lambda-Cyhalothrin and Deltamethrin

Lambda-cyhalothrin (LC) (($R+S$)-α-cyano-3-(phenoxybenzyl($1S+1R$)-*cis*-3-(*Z*-2-chloro-3,3,3,-trifluoroprop-1-enyl)-2,2-dimethyl-cyclopropane-carboxylate) and deltamethrin (DM) (cyano(3-phenoxyphenyl)methyl-3-(2,2-dibromoethenyl)-2,2-dimethyl-cyclopropane-1-carboxylate), are pyrethroids insecticides.

LC was firstly reported in 1984 by Robson and Crosby and 1 year later it was introduced by ICI Agrochemical (now Syngenta) (He et al. 2008).

DM, is fourth generation synthetic pyrethroid pesticide and belongs to an α-cyano, type II pyrethroids. It was obtained by Elliott in 1974 and has been commercialized since 1982 (Pavan et al. 1999; Koprucu and Aydm 2004).

LC and DM are used in agriculture against a broad spectrum of insect pests of economically important crops. They are also used for the control of household insect pests such as mosquitoes, cockroaches, flies, termites, and fleas. Both of them exhibit low mammal toxicity (Tabaeran and Narahashi 1998).

Despite the similar structures of LC and DM, the first one is resistant to degradation in soil, while the second is not. Both of them are photostable and very resistant to hydrolysis in aquatic system. It results from their lipophilic properties. In water sediments system they are decomposed fast. They are biodegradable (Tabaeran and Narahashi 1998).

Physical and chemical properties of LC and DM, including their half-lives in soil and water are listed in Table 2 (Source: The PPDB).

5.1 Abiotic Degradation of Lambda-Cyhalothrin

5.1.1 Hydrolysis of Lambda-Cyhalothrin

LC is stable in acidic solution, in alkaline conditions it is hydrolyzed since it is a lipophilic compound. It results from presence of α-cyano benzyl moiety (II pyrethroid class), which causes alkaline hydrolysis acceleration (He et al. 2008; Katagi 2002).

The mechanism of LC hydrolysis is based on nucleophilic attack of the hydroxyl ion (Fig. 8) (He et al. 2008).

As a result, a cyanohydrin derivative (B) was formed, which was unstable and transformed into acidic derivative (D) and hydrocyanic acid (E) (He et al. 2008).

Because of LC lipophilic properties, its strong adsorption to soil and low risk of water contamination, most studies focused on photodegradation and biodegradation this compound in soil.

5.1.2 Photodegradation of Lambda-Cyhalothrin

LC exposure to UV light (254 nm) resulted in nearly complete degradation with losses of more than 95 % of the initial amount. According to He et al. (2008) the pathways of LC photodegradation included decarboxylation, reductive dehalogenation and ester or other bond cleavage. These processes are presented in Fig. 9.

Compounds: B (3-(2-chloro-3,3,3,-trifluoroprop-1-en-1-yl)-2,2 dimethylcyclopropanecarboxylic acid) and D ((3-phenoxyphenyl)acetonitrile) were products of LC ester bond cleavage (A). Moreover, compound D can be also

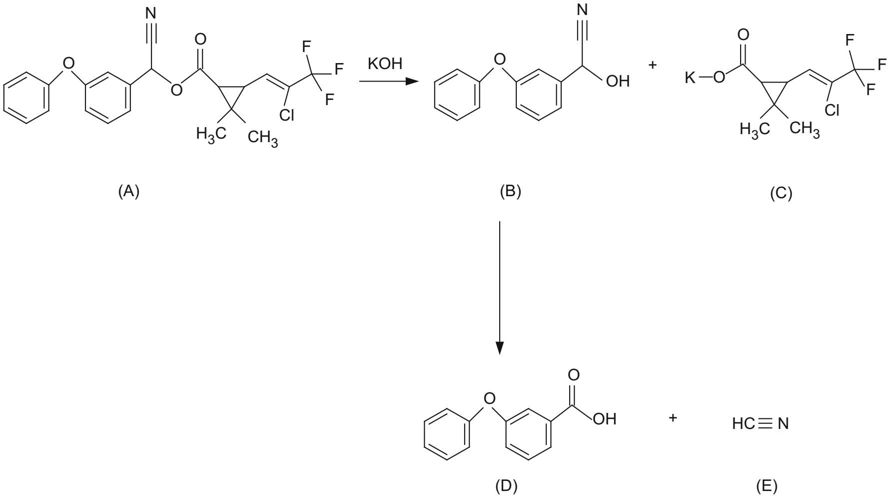


Fig. 8 Hydrolysis of LC in alkaline conditions

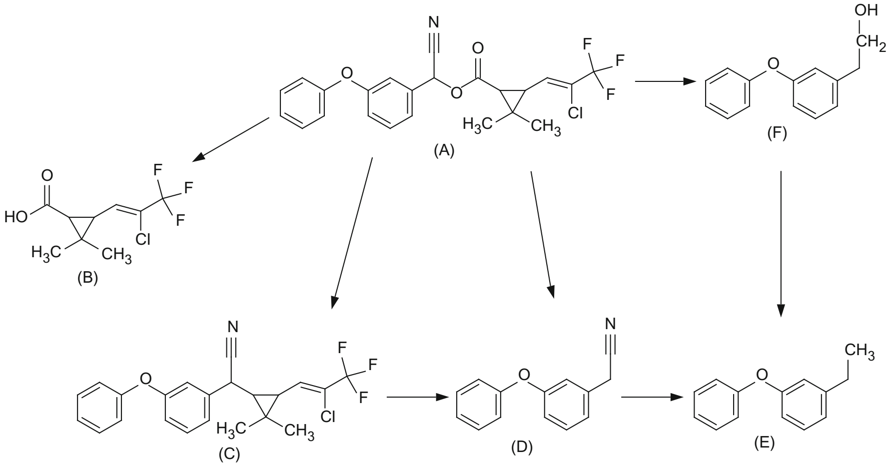


Fig. 9 Photodegradation of LC

generated by cleavage of C-C bond of compound C (decarboxyhalothrin), which was formed through the decarboxylation pathway. Photoproduct F ((3-phenoxyphenyl)methanol) was formed by the ester cleavage and subsequent loss of the cyano group of LC and photoproduct E (1-methyl-3-phenoxybenzene) was formed by hydroxyl or cyano group loss from compounds D or F (He et al. 2008).

In soil surfaces and in aqueous solutions at pH = 5, LC was degraded in the presence of sunlight with a half-life of 30 days. The degradation in soil occurred through hydroxylation followed by cleavage of the ester linkage resulting in two main degradation products that were finally degraded to carbon dioxide.

LC has a low potential to contaminate groundwater because of its low water solubility and high potential to bind to soil. Studies on microbial activity of *Pseudomonas fluorescens* and *Trichomonas viridiae* revealed that concentration of LC decreased in the presence of these microorganisms and sunlight (Manigandan et al. 2013).

In order to identify the LC photodegradation pathways and their mechanisms, Liu et al. (2014a, b) examined LC photochemical decomposition in solution under laboratory conditions. They used two light sources: Hg and Xe lamp, which were characterized by different emission spectrum: ultraviolet region and 800–1000 nm range, respectively. Exposition of LC solution to ultraviolet radiation accelerated its photodegradation, because chemical bond energy of LC, like other pyrethroids, was below energy corresponding to ultraviolet region. Moreover, it was proven that LC photodegradation fitted to first-order kinetics and were performed through ester, C-C and C-O cleavage, photooxidation (mostly), photoisomerization and decyanation. The major products of these processes were: 3-phenoxybenzaldehyde, 3-phenoxybenzoic acid methyl ester, 4-phenoxybenzoic acid and m-phenoxybenzoic acid, and two other of products, which were not identified.

In order to remove organic compounds from water, advanced oxidation processes (AOP) are used, which include photo-Fenton reaction. It is based on the ferric hydroxyl complex $Fe(OH)^{2+}$ photolysis and generation of ferrous ions and hydroxyl radicals, that accelerated organic compounds degradation (Colombo et al. 2013).

This reaction was used to evaluate the efficiency of LC degradation in aqueous solution by Colombo et al. (2013). They conducted simultaneous LC hydrolysis and photolysis in the absence of ferrous sulfate and hydrogen peroxide under UV light irradiation at $pH = 6.2$ and 2.5 (hydrolysis) and at $pH = 2.5$ (photolysis). Results showed, that for photo-Fenton reaction, about 85 % of LC initial concentration was degraded, but during hydrolysis and photolysis only 10 and 17 % of initial pesticide concentration was degraded, respectively. They revealed that photo-Fenton reaction enabled efficient reduction in the concentration of LC in the environment.

The LC photodegradation by solar photo-Fenton was also tested, based on Fenton reaction ($Fe^{2+} + H_2O$), which formed hydroxyl radicals and iron oxidation (first experiment), and solar photo catalysis (UV/TiO2) (second experiment). The LC degradation process was more efficient in the first experiment (removal of 80.65 % of initial concentration of LC) than in the second one (63.7 %) (Alalm et al. 2015).

5.2 *Biodegradation of Lambda-Cyhalothrin*

Due to the fact that LC is an ester compound and consists of acid and alcohol moiety, it is susceptible to esterase activity. Therefore, it esterase gene pytY was isolated from the genomic library of *Ochrobactrum anthropi* YZ-1 and its activity was tested. An enzyme assay described by Ruan and coworkers (2013) showed, that this enzyme was able to degrade various pyrethroids, including LC. This process is influenced by pH and temperature, since these parameters effect esterase activity.

PytY showed the highest activity at pH and temperature in the range of 5.0–9.0 and 15–45 °C respectively. Its activity decreased when pH exceeded 7.5 and temperature was higher than 45 °C (Ruan et al. 2013).

Some research on LC biodegradation indicated that it is used as carbon and nitrogen source by microorganisms in soil (Peackock et al. 2014; Chen et al. 2015).

Soil rhizosphere microorganisms are capable to use LC as a carbon source, as was shown by Peackock et al. (2014), who applied a redox gradostat reactor for measurement of microbial activity of LC.

Shen and coworkers (2015a, b) conducted studies on LC degradation in sterile and non-sterile soils under laboratory conditions. Results revealed longer LC half-life in sterile soil than in presence of soil microorganisms. In sterile soil the half-life was around 161 days, in non-sterile soil the average half-life was around 120 days. They also observed longer LC half-life at low pH and reduced exposure to light. Under field conditions, LC half-lives were also longer than under laboratory conditions, what suggested the dependence of LC degradation in soil on pH, temperature, exposure to light and microbial activity (Wang et al. 1997; Laabs et al. 2000).

Chen et al. (2015) performed a detailed study of LC degradation pathways by *Bacillus thuringiensis* strain ZS-19. It was proven, that this process was highly effective since the bacterium used this pesticide as a source of carbon and nitrogen, similar to rhizosphere microorganisms.

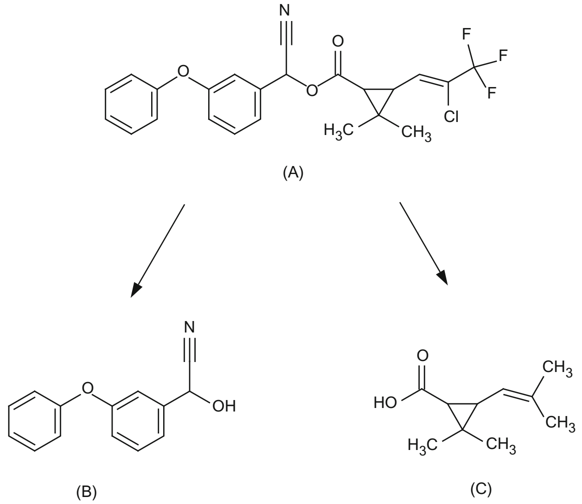
Pathway of LC biodegradation is presented in Fig. 10.

Degradation is initiated by the cleavage of the carboxylester linkage through hydrolysis, which is the main pathway of LC (A) degradation. Metabolites are: α-hydroxy-3-phenoxy-benzeneacetonitrile (B) and (1R,3R)-trans-2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropane-1-carboxylic acid (C) (Chen et al. 2015).

Compound B is also formed in alkaline hydrolysis LC (Sect. 5.1.1, Fig. 8), which indicates that in these microorganisms hydrolysis also occurs.

As shown in Fig. 11 main metabolites are produced by cleavage of the diaryl bond and aromatic ring of compound B. These metabolites are: 3-phenoxy-

Fig. 10 Pathway of LC degradation by *Bacillus thuringiensis* strain ZS-19



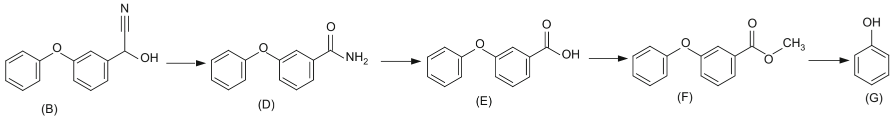


Fig. 11 Transformation of α-hydroxy-3-phenoxy-benzeneacetonitrile, one of LC metabolite

benzamide (D), 3-phenoxybenzoic acid (E), 3-phenoxybenzoate (F) and phenol (G) (Chen et al. 2015).

This pathway confirms that cyanohydrin derivative was unstable, as mentioned in Sect. 5.1.1. Its hydrolysis and biodegradation products were similar, which suggested that *Bacillus thuringiensis* strain ZS-19 could also perform hydrolysis (Chen et al. 2015).

5.3 Toxicity of Lambda-Cyhalothrin

Since LC is a chiral compound, the particular attention of researchers is drawn to determining the toxicity of its enantiomers. Since synthetic pyrethroids have endocrine disruptive properties, their possible influence on the functioning of the endocrine system is investigated, including reproductive as well as its neurobehavioral toxicity (Ansari et al. 2012; Yousef 2010). Assessment of LC toxicity to different organisms was the object of many investigators (Fetoui et al. 2009; Jalali et al. 2009; Kolo et al. 2010).

(−)-LC exhibited higher activity (determined by measuring the cell proliferation, cell viability, apoptosis, and receptor gene expression) (Zhao and Liu 2009; Zhao et al. 2010) then the (+) isomer.

The bioavailability and enantioselectivity differences between LC isomers in earthworm (*Eisenia fetida*) were investigated. Compound sorption on soil plays an important role in bioavailability for earthworm. The bioaccumulation of LC was found to be enantioselective in this organism. Earthworms took up LC enantioselectively, preferentially accumulating the less toxic enantiomer. The more toxic enantiomers ((−)-LC) was preferentially degraded in earthworm and led to less toxicity on earthworm for racemate exposure (Chang et al. 2016).

5.4 Abiotic Degradation of Deltamethrin

5.4.1 Hydrolysis of Deltamethrin

DM, similar to LC, is stable in acidic solution, in alkaline conditions it is hydrolyzed since it is a lipophilic compound. The α-cyano benzyl moiety (II pyrethroid class) accelerates alkaline hydrolysis. Due to DM low water solubility (Table 2), the hydrolysis does not occur.

5.4.2 Photodegradation of Deltamethrin

DM, like other pyrethroids, contains double bonds that are unstable after exposure to light, therefore these compounds are susceptible for photodegradation in the environment. Among the main degradation processes: hydrolysis, biodegradation and photodegradation, the latter one is prevailing. Possible pathways for the DM photodegradation under laboratory conditions were proposed by Liu et al. (2009). Photodegradation of DM is presented in Fig. 12.

According to Liu and coworkers (2009) DM (A) is degraded by ester cleavage; as a result photoproduct B is formed. Subsequently decyanation occurs, resulting in a formation of 3-phenoxybenzalcohol (compound C). This photoproduct is afterwards degraded in the photooxidation process to photoproducts E and F.

Similar results were obtained by Nahri-Niknafs and Ahmadi (2013). They investigated the degradation of pyrethroid insecticides: DM and fenvalerate in natural

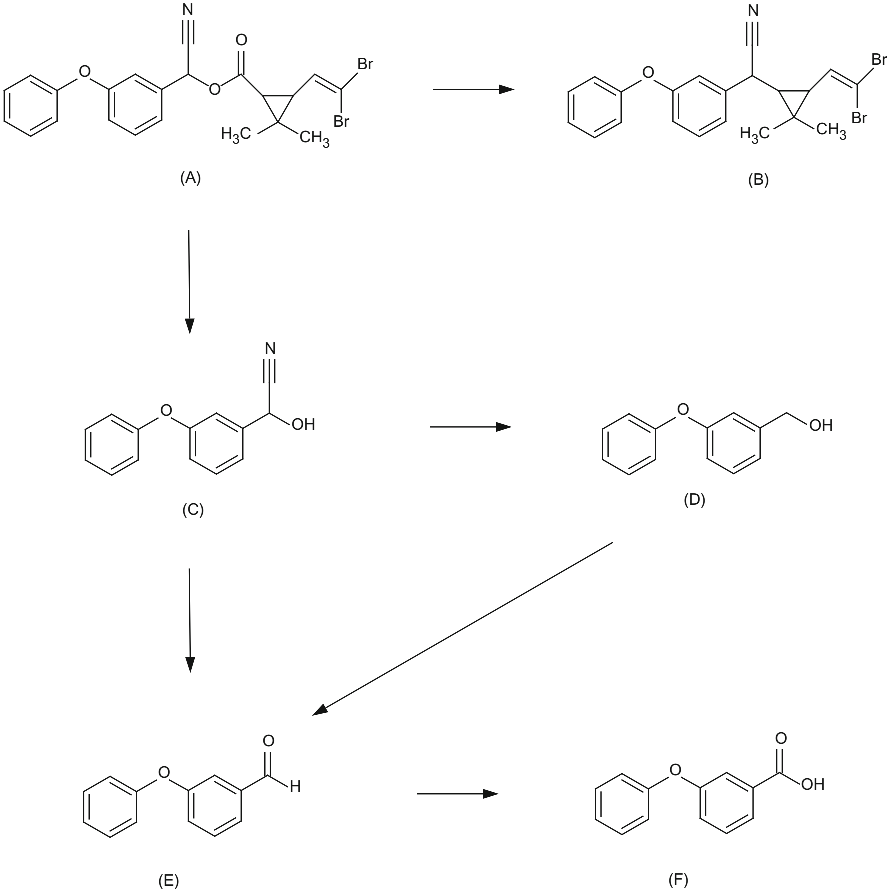


Fig. 12 Photodegradation of DM

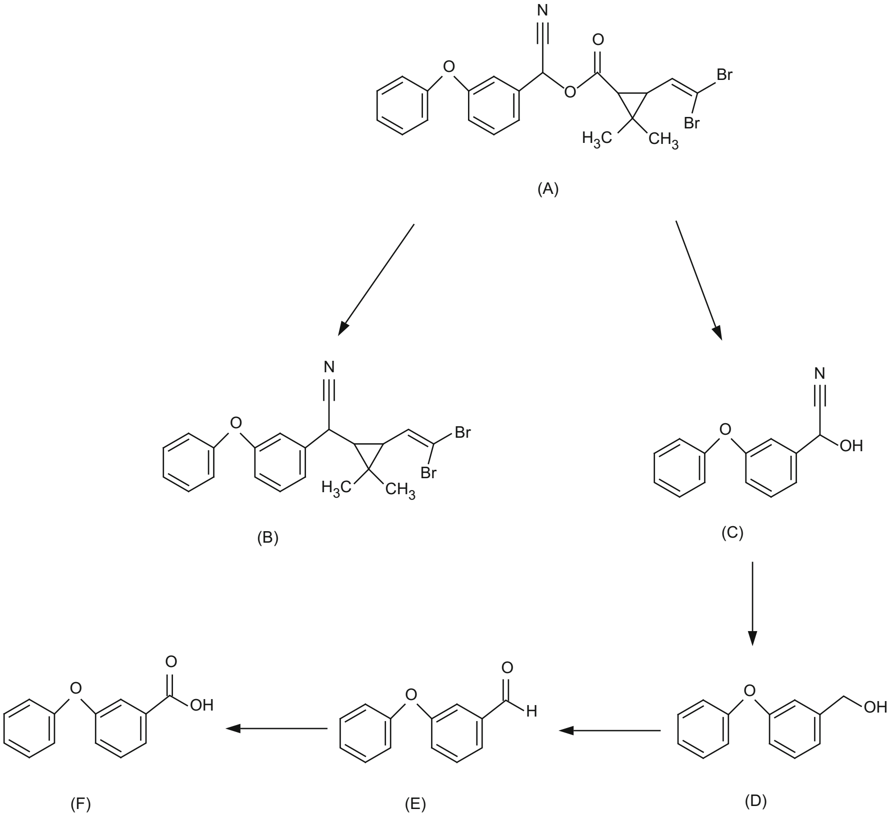


Fig. 13 Proposed pathway of DM photodegradation

river water under simulated solar light. Four types of reactions were observed: ester cleavage, photooxidation, photoisomerization (only for fenvalerate) and decyanation. Proposed pathways of DM photodegradation are presented in Fig. 13.

Compound C—hydroxyl 3-phenoxyphenyl acetonitrile—is obtained by ester cleavage of DM (compound A). Subsequently compound C is transformed to 3-phenoxy benalcohol (compound D) by DM decyanation. Result of derivative D photooxidation is photoproduct E—3-phenoxy benzaldehyde. The last compound F, 3-phenoxybenzoic acid, is generated by photooxidation of compound E (Nahri-Niknafs and Ahmadi 2013).

5.5 Biodegradation of Deltamethrin

Studies on the microbial transformation of the five pyrethroid insecticides: permethrin, deltamethrin, fastac, fenvalerate, fluvalinate revealed that in microbial culture, composed of *Bacillus cereus*, *Pseudomonas fluorescens* and

Achromobacter sp., DM was the most persistent among all of the investigated pesticides (Maloney et al. 1988).

The first DM-degrading bacterium strain was isolated in 1988, but it was not able to completely decompose this pesticide, because of toxic effects of the major product of this process to this microorganism (Chen et al. 2011).

Devisri and Iyer (2013) isolated from Koovar river water microorganisms: *Bacillus sp*, *Klebsiella sp*, *Pseudomonas sp* and *Staphylococcus sp*, which were able to biotransform DM.

Because of DM's lipophilic properties, it is characterized by strong adsorption to soil organic matter, and therefore low mobility in soil. Nevertheless, DM can degrade by soil microorganisms and photolysis. These processes mainly depend on soil type and oxygen availability.

According to studies described in (Grant et al. 2002; Cycoń et al. 2014) a bacterium *Serratia marcescens* strain DeI-1 and DeII 2 uses DM as a source of carbon and energy. Strain DeI-1 was more effective than DeII-2, which results from the higher sensitivity of the first strain to DM degradation product—3-phenoxybenzaldehyde.

Zhang et al. (2016) proved, that DM biodegradation depended on pH and temperature. Results indicate faster degradation in neutral and alkaline conditions because of lower enzyme activity in acidic conditions. The rate of biodegradation decreases at high temperature (40 °C), while enzyme activity decreases at low temperature (15 °C), as the bacterial growth is slower. Higher degradation rate is observed in soils containing *Bacillus cereus* strain Y1, in comparison to sterilized soil. It was also suggested that this bacterium strain could be applied in bioremediation processes.

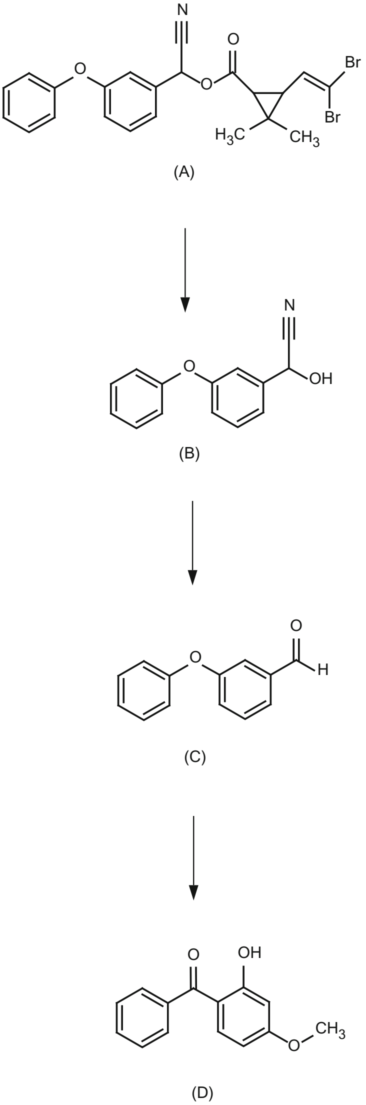
Another bacterium, which is capable of complete degradation of DM and other pyrethroids, e.g. cypermethrin or permethrin is *Streptomyces aureus* strain HP-S-01. Degradation of DM was the most efficient in 18–38 °C temperature range and at pH in the range of 5–10 (Chen et al. 2011). Moreover, this pyrethroid pesticide could be also transformed by the following bacterium: *Micrococcus sp* (Tallur et al. 2008), *Brevibacterium aureum* (Chen et al. 2013), *Pseudomonas aeruginosa* strain JQ-41 (Song et al. 2015) and *Bacillus subtilis* strain BSF01 (Xiao et al. 2015).

As presented in Fig. 14, DM (A) is degraded by hydrolysis of carboxylester linkage to α-hydroxy-3-phenoxy-benzeneacetonitrile (B). This product is unstable and quickly transforms into 3-phenoxybenzaldehyde (C), which is subsequently degraded to 2-hydroxy-4-methoxybenzophenone (D). The major product of DM biodegradation is 3-phenoxybenzaldehyde (Chen et al. 2011).

5.6 Toxicity of Deltamethrin

DM is a chiral compound. Its toxicity depends on its stereochemical structure. Investigations show, that this pyrethroid insecticide is highly toxic to aquatic organism because it is easily washed from land into surface water. The WHO

Fig. 14 Pathway of DM biodegradation by *Streptomyces aureus* strain HP-S-01



(World Health Organization) issued a report about the high toxicity of DM to fish (Ural and Saglam 2005; Tuzmen et al. 2008).

DM shows an adverse effect on the fecundity of the females of *Lysiphlebus fabarum Marshall* (Maradani et al. 2016). DM induced a significant rise in levels of oxidative stress in earthworms (*Eisenia foetida*), increasing the production of peroxidation products (malondialdehyde and protein carbonyls) and increasing the comet assay tail DNA% (determined by single-cell gel electrophoresis) (Shen et al. 2015a, b).

Abdel-Daim and coworkers (2016) examined the potential hepatoprotective, nephroprotective, neuroprotective and antioxidant effects of DM toxicity in male mice. Oral exposition of mice to DM revealed a significant increase in serum hepatic and renal injury biomarkers as well as TNF-a level and AChE activity. Moreover, liver, kidney and brain lipid peroxidation and oxidative stress markers were altered due to DM toxicity.

The teratogenicity of a DM solution and Decis® (an insecticide formulation containing DM) in chick embryos was investigated by Bhaskar and coworkers (2012, 2015).

Eggs of *Gallus domesticus* were immersed in aqueous emulsions of DM as well as Decis solution and incubated. After incubation the recovered embryos were evaluated for mortality rate, wet body weight, gross morphological and skeletal malformations. The result revealed that embryonic mortality markedly increased after administration of DM. The significant decrease in wet body weight and significant increase in percentage of abnormal survivors was observed in a dose dependent manner. A spectrum of external and skeletal malformations was observed in DM treated embryos. Among biochemical changes, total glycogen and RNA contents were significantly decreased in embryos exposed to DM. Similarly, a significant alteration was observed in alanine transaminase activity. These findings suggests that DM exhibits embryotoxic and teratogenic effects in the developing chick embryos.

6 Rimsulfuron

Rimsulfuron (RIM), N-((4,6-dimethoxypyrimidin-2-yl)aminocarbonyl)-3-(ethylsulfonyl)-2-pyridine-sulfonamide, is a herbicide of the sulfonylurea class. It was commercialized in 90s by Du Pont de Nemours (Martins et al. 2001).

It controls growth of grasses and some broadleaf weeds. This sulfonylurea herbicide is applied on corn crops at the 2–6 leaves stages. It can be also applied alone or in mixture with metribuzin (selective herbicide of the same chemical class as triazines) in potato crops. It is absorbed by the leaves and roots of the plants (Rouchaud et al. 1997).

RIM, like other sulfonylureas, quickly became popular because of low application doses and favorable environmental and toxicological properties (Nageswara Rao et al. 2012).

Rimsulfuron is a weak acid (see pKa in Table 2). Its molecule contains an aryl group, a sulfonylurea bridge and a heterocycle derived from triazine (Martins et al. 2001). Introduction of chlorine in the herbicide molecule enhances the stability of these compounds and prolongs their activity in the environment.

Its stability in the environment is low; it rapidly degrades in water and soil and it does not pose a risk to the environment. However, it is important to monitor pathways of its degradation, because derivatives can be more toxic than the parent compound. In soil under field conditions its decomposition is faster than under laboratory conditions. It results, like for TMX, from higher microbial activity and additional exposure to light. It is moderately fast degraded in aquatic system by photolysis. RIM has polar properties (see solubility in water at 20 °C and logP in Table 2) and it is not resistant to hydrolysis. It is also rapidly decomposed in water sediment systems and does not cause contamination of water (Martins et al. 2001; Seńczuk 2005). It has little or no toxological effects on mammals (Scrano et al. 1999).

Physical and chemical properties of RIM, including its half-lives in soil and water are listed in Table 2 (Source: The PPDB).

6.1 Abiotic Degradation of Rimsulfuron

6.1.1 Hydrolysis of Rimsulfuron

Hydrolysis of sulfonylurea herbicides like RIM in aqueous solutions proceeds according to first-order kinetics, and depends on pH and temperature. Hydrolysis under acidic conditions is based on cleavage of the sulfonylurea bridge. The following degradation products were identified: sulfonamide, the heterocyclic amine and carbon dioxide. Since these compounds are weak acids, in neutral and alkaline conditions they are much less likely to undergo hydrolysis (more persistent to hydrolysis). The rate of hydrolysis at pH above 10 increases due to base-catalyzed reaction mechanism. It was also proven, that with increases of temperature, stability of this compound to hydrolysis decreases. These studies were conducted under laboratory conditions, but the same results were obtained under field conditions (Kearney and Kaufman 1969).

6.1.2 Photodegradation of Rimsulfuron

Schneider and coworkers (1993) showed that RIM degradation in aqueous neutral solutions and in soil does not depend on irradiation. In acidic conditions ($pH = 5$) they observed photodegradation of RIM. The same conclusions were reached by Scrano and coworkers (1999). They also observed that exposure to light did not affect the rate of degradation under neutral and alkaline conditions. Simultaneously, it was shown that hydrolysis conducted under sunlight is faster in acidic or alkaline conditions, than neutral.

Under simulated sunlight in water, at pH 5 and 9, the photodegradation half-life was in the range of 1–9 days. The hydrolysis rate was as high as the photolysis rate and both decrease with increasing pH. The pathway of RIM degradation in neutral and alkaline conditions is presented in Fig. 15 (Scrano et al. 1999).

RIM was degraded to N-(4,6-dimethoxy-2-pyrimydinyl)-N-[(3-(ethylsulfonyl)-2-pyridynyl)]urea (B) and N-[(3-ethylsulfonyl)-2-pyridynyl]-4,6-dimethoxy-2-pyridineamine (C) under neutral and alkaline conditions. The major metabolite

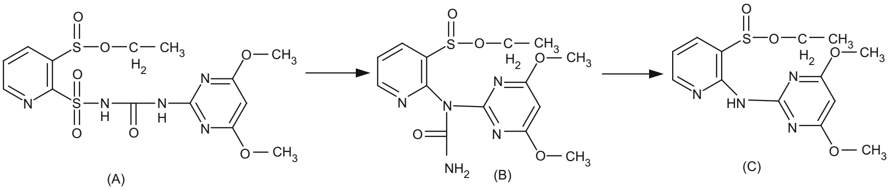


Fig. 15 Abiotic degradation of RIM in neutral and alkaline conditions

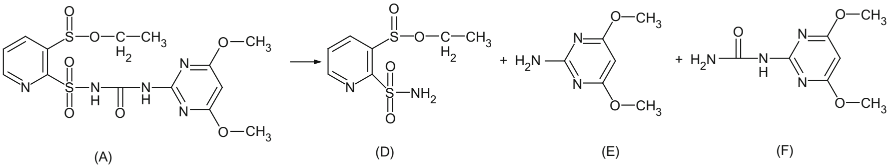


Fig. 16 Abiotic degradation of RIM in acidic conditions

under these conditions was compound C, which was more stable than compound B (Scrano et al. 1999).

Hydrolysis in acidic solutions ($pH < 7$) was also observed. The main pathway of RIM abiotic degradation under acidic condition is presented in Fig. 16 (Scrano et al. 1999).

The major metabolites of RIM (A) under acidic conditions were: 3-(ethylsulfonyl)-2-pyridinesulfonamide (D), 2-amino-4,6-dimethoxypyrimidine (E) and N-(4,6)-dimethoxy-2-pyrimidynyl)urea (F) (Scrano et al. 1999).

Martins and Marmoud (1999) conducted experiments on RIM degradation in aqueous solutions and soil suspensions. They observed, similar to above-mentioned scientists, that this herbicide was rapidly degraded with the same rate in both environments and its degradation rate depended on pH. They revealed that derivative B (Fig. 15) is also persistent in soil.

In distilled water containing KOH ($pH = 10$) Martins and coworkers (2001) also observed that RIM is hydrolyzed to compound C (Fig. 15). These studies confirmed the similar hydrolysis sensitivity of metabolite B to RIM and the higher persistence of compound C than the parent compound, which could pose a risk for groundwater contamination. They observed a higher rate of RIM degradation in aqueous soil suspensions under field conditions than in water. Moreover, it was shown that the initial concentration of RIM also influences the degradation processes of its metabolites. These investigations revealed a higher rate of metabolite C degradation for the low concentration of parent compound, while it was not observed for metabolite B (Fig. 15). It was explained by inhibition of microbial activity at high concentrations.

Metabolism of RIM in soil was also examined by Rouchaud and coworkers (1997). RIM transformation undergoes intramolecular nucleophilic substitution.

As a result, derivative B is obtained, which subsequently is converted to amine (compound C) by extrusion of SO_2NHCO group. They proved that 2-hydroxypyridine was more stable than RIM. 2-amino-4,6-dimethoxypyrimidine was also detected but its concentration was lower than 2-hydroxypyrimidine. These compounds were products of a second pathway of RIM degradation via nucleophilic substitution by OH^- at the 2-pyridine carbon atom and sulfonyl bridge breakage. These results were partially confirmed by Schneider et al. (1993), who observed only compounds B and C.

6.2 Biodegradation of Rimsulfuron

There are some types of microorganisms, which are capable to degrade sulfonylurea herbicides: actinomycetes, fungi and bacteria. *Streptomyces griseolus*, belongs to acinetomycetes, degraded chlorsulfuron via conversion of the methoxy to hydroxyl group. *Aspergillus niger* and *Penicillium sp.* (fungi) were able to hydrolyze the sulfonylurea bridge. Sulfonamide and heterocyclic compounds were the products of this reaction. Two degradation pathways of RIM (Fig. 17) were proposed, similarly to other sulfonylurea herbicides (Kearney and Kaufman 1969).

According to Song et al. (2013) RIM, as well as others sulfonylurea herbicides: tribenuron methyl, chlorsulfuron, bensulfuron methyl, methametsulfuron methyl, cinosulfuron and nicosulfuron, were degraded by *Talaromyces flavus*, strain LZM1. These fungi probably used RIM as a nitrogen source, since the pathways of RIM's degradation occurred via cleavages of N-containing bonds.

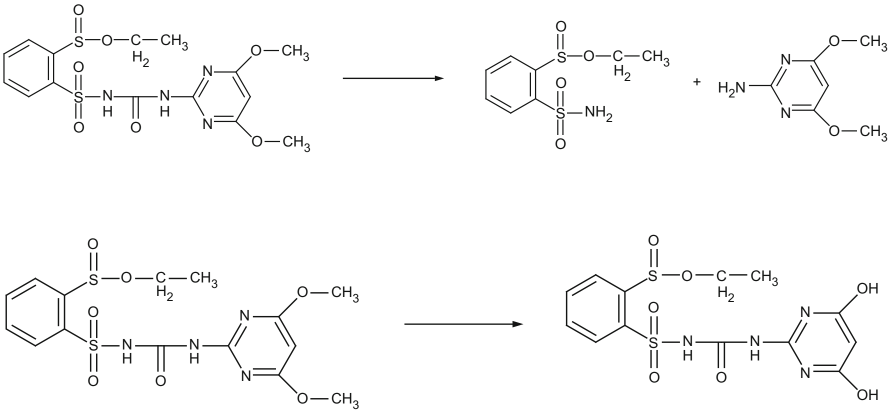


Fig. 17 The possible biodegradation pathway of RIM

6.3 Toxicity of Rimsulfuron

In the environment RIM decomposes to five degradation products, the major two of them are: [N-(4,6-dimethoxypyrimidin-2-yl)-N-((3-ethylsulfonyl)-2-pyridinyl) urea] and [N-((3-ethylsulfonyl)-2-pyridinyl)-4,6-dimethoxy-2-pyrimidineamine], both of which are more stable in the environment than the parent compound (380–1100 days, 101–214 days for metabolites, respectively and 6–40 days for parent compound) (EFSA 2005; Rosenbom et al. 2010).

The herbicidal activity of RIM is specific to plants, however, its degradation products are not herbicides and they may be less toxic to algae than the parent compound, therefore the toxicity test was conducted with *D. manga* and *V. fischeri*. The assessment of the toxicity of RIM and their major degradation products was the object of Martins and coworkers' investigations. At the maximum tested concentration, RIM and its major degradation products were toxic neither to *Dapnia manga* nor to *Vibro fischeri* (Martins et al. 2001).

The toxicity of RIM and other sulfonylurea herbicides towards *Lemna gibba* was investigated at three pH levels, at two temperatures and two light regimes. In all cases RIM exhibited toxicity to *Lemna gibba*, however the EC50 values were different for different experimental conditions (Rosenkrantz et al. 2013).

Risk assessment of RIM and its primary degradation products indicates adverse effects on earthworms (long-term), non-target terrestrial plants and aquatic plants (EFSA 2005; Rosenbom et al. 2010).

Dinelli and coworkers (1998) ascertained, that a high concentration of rimsulfuron in soil (5 mg/kg) resulted in a transient increase of both respiration and dehydrogenase activity.

7 Metalaxyl

Metalaxyl (MET), *N*-(2,6-dimethylphenyl)-*N*-(methoxyacetyl)alanine methyl ester, is a pesticide, which belongs to phenylamide fungicides. It was first manufactured in 1977 by the Ciba-Geigy Corporation (Zuno-Floriano et al. 2012).

(−)-R-metalaxyl is the biological active enantiomer, which acts by inhibiting the synthesis of ribosomal RNA in the fungus. Since 1996 in most countries, rac-metalaxyl is replaced by metalaxyl-M ((−)-R-metalaxyl) (Xu et al. 2011).

MET is a systemic fungicide, which is adsorbed by roots, translocated and extensively metabolized by plants (Zuno-Floriano et al. 2012).

Application of MET allows protecting potato from *Peronosporales*, especially *Phytophthora infestans*, a pathogen, which affects leaves, stems and tubers of potatoes, but does not affect their growth. It inhibits uridine incorporation into RNA by interfering with transcription. Specifically it inhibits RNA polymerase-1 of the fungi and blocks rRNA synthesis (Sharma and Awasthi 1997; Sukul and Spiteller 2000; Zuno-Floriano et al. 2012). In soil MET is moderately resistant to decomposition. It is also a heat resistant and photostable compound. It exhibits high stability in aqueous solutions within 1–8.5 pH range. At higher pH (e.g. 10) it decomposes faster and degrades rapidly in water, like other fungicides (Sukul and Spiteller 2000; Katagi 2002). In water sediments systems, it is moderately fast degraded and its half-life is about 56 days.

MET does not affect reproduction of animals and is not a teratogenic or mutagenic compound but it provokes cell alterations in mouse liver at the dose of 2.5 mg/kg/day; in dogs at dose of 0.8 mg/kg/day. It alters alkaline phosphatase levels in blood and causes an increase in liver and brain weight (Zuno-Floriano et al. 2012).

Physical and chemical properties of MET, including its half-lives in soil and water are listed in Table 2 (Source: The PPDB).

7.1 Abiotic Degradation of Metalaxyl

7.1.1 Hydrolysis of Metalaxyl

MET possesses an amide linkage moiety, which is resistant to hydrolysis in aquatic systems. Nevertheless, it undergoes degradation under acidic and alkaline conditions with half-lives of 200 and 115 days, respectively (Sukul and Spiteller 2000).

According to Katagi (2002), in acidic conditions, as a result of H_2O attack on the O-protonated carbonyl carbon, a tetrahydral intermediate is formed. Water-assisted C-N fission is an effect of protonation at the amide nitrogen. Alkaline hydrolysis is initiated by nucleophilic attack of the hydroxide on the carbonyl carbon, which leads to the formation of monoanionic tetrahydral intermediate. Proposed pathways of these reactions are presented in Fig. 18.

7.1.2 Photodegradation of Metalaxyl

As MET does not absorb light above 290 nm (it has maximum absorption at 196 nm), it is resistant to sunlight (Sukul and Spiteller 2000).

Photolysis of MET in UV light leads to rearrangement of the N-acyl group into an aromatic ring, demethoxylation, N-deacylation and elimination of the methoxycarbonyl group from the molecule. In the presence of aerobic organisms dwelling in humic acids, 65 % of metalaxyl is degraded. Humic acids, present in soil, produce OH radicals, which could degrade MET. Therefore, in the absence of humic acids photodegradation of MET does not occur (Sukul and Spiteller 2000).

MET degrades in aqueous solution in pH range from 2.8 to 8.8 exposed to UV light. The lower pH of the solution the rate of degradation is higher (Sukul and Spiteller 2000).

Marucchini and coworker (2002) investigated the stereoselective degradation of MET (as racemate) and MET-M (as (−)-(R)-enantiomer) in soil. The obtained

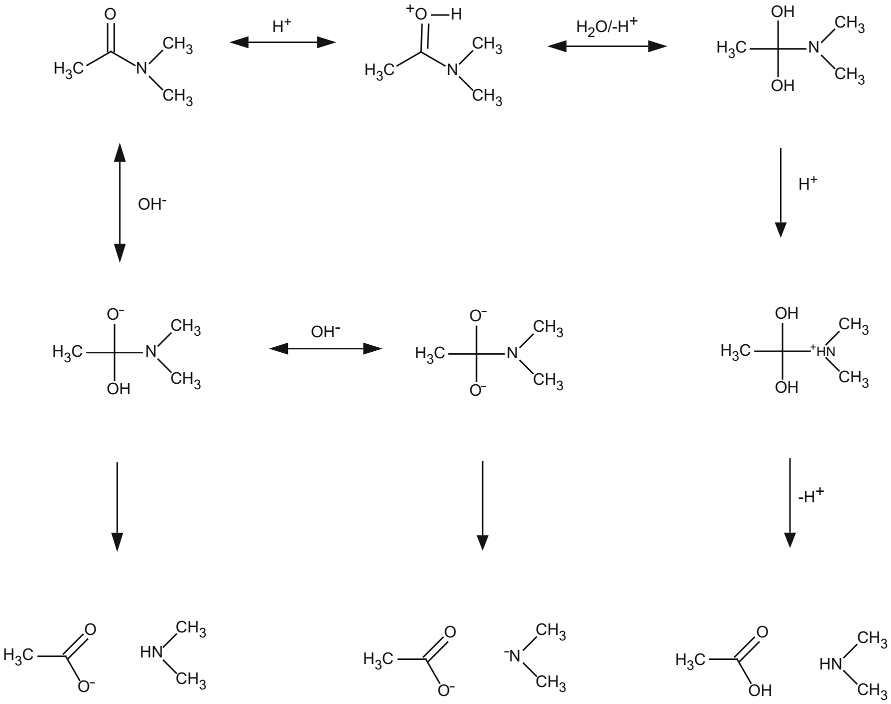


Fig. 18 MET hydrolysis

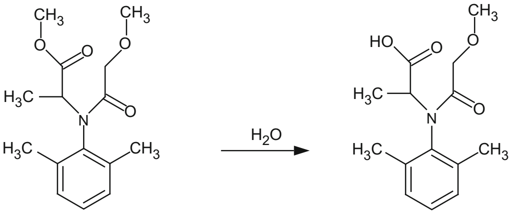
half-lives in soil were 25 and 43 days respectively, which indicated that MET was faster degraded than MET-M. The same studies proved faster (−)-(R)-enantiomer degradation (half-life 17 days) in comparison to (+)-(S)-enantiomer (half-life 61 days).

7.2 Biodegradation of Metalaxyl

One of the first investigations obtained by Bailey and Coffey (1985) showed that MET biodegradation occurred in soil. MET was stable in sterilized soil and its concentration was only about 10 % lower in comparison to the initial concentration 70 days earlier. In unsterilized soil it was degraded faster and the average half-life was 28 days, but for the most active soil it was 14 days. These results suggested that MET undergoes biodegradation processes.

Studies conducted by Massoud et al. (2008) showed that *Pseudomonas sp* (ER2) is the most effective bacteria for MET degradation in aquatic systems. Therefore, it is used for detoxification of water contaminated with MET. According to (Massoud et al. 2008) there were also three fungi species, that took part in MET degradation:

Fig. 19 MET hydrolysis in plants



Aspergillus niger (ER6), *Cladosporium herbarum* (ER4) and *Penicillium sp* (ER3). These microorganisms exhibited the highest activity at pH 7 and temperature 30 °C (optimum conditions). It results from the fact that the optimal pH for fungal and bacteria growth is 6–8.

Acinetobacter sp, a common soil microorganism, is one of bacterium species, which is able to degrade MET. Density of *Acinetobacter sp* cells in the treated potato seedlings with MET was higher than in the control group (Zuno-Floriano et al. 2012).

The main product of MET biodegradation is metalaxyl acid. It suggests that microorganisms transform this pesticide by hydrolysis, similar to plants (see Fig. 19).

MET can be also degraded in plants and animals by cleavage of the ester and a concurrent series of oxidative biotransformations (dealkylation, alkyl and aryl hydroxylation). In plants, MET is mainly hydrolyzed to its carboxylic acid metabolite—metalaxyl acid (Li et al. 2013).

A scheme of hydrolysis metalaxyl in plants is shown in Fig. 19.

Because of MET chirality, many studies are dedicated to enantioselective degradation of this fungicide. Therefore, Sulimma and coworkers (2013) investigated the enantioselective degradation of chiral fungicides: MET and furalaxyl. They discovered that only one strain of *Bacillus brevis*—INFU/LS_S1 is able to enantioselectively transform rac-metalaxyl. They also detected (−)-R-acid at higher concentration in the experimental medium (pH = 7.4) which suggests faster degradation of (−)-R-metalaxyl. It is important due to the fact that currently used agrochemicals consist of (−)-R-metalaxyl, which has higher fungicidal activity. Proposed MET metabolites are presented in Fig. 20.

Moreover, obtained results confirmed, that metabolism of MET is an enantioselective process: R-metalaxyl was degraded to pure R-metalaxyl acid and S-metalaxyl was degraded to pure S-metalaxyl acid by bacteria (Sulimma et al. 2013; Kalathoor et al. 2015). The same results were obtained by Li and coworkers (2013).

The R- and S-enantiomers of MET were also determined in cucumber, cabbage, spinach and pakchoi. The results showed that in cucumber R-enantiomer dissipated faster than S-enantiomer. Inversely, a preferential degradation of S-form was found in spinach and pakchoi. In cabbage no stereoselective degradation was observed (Wang et al. 2014).

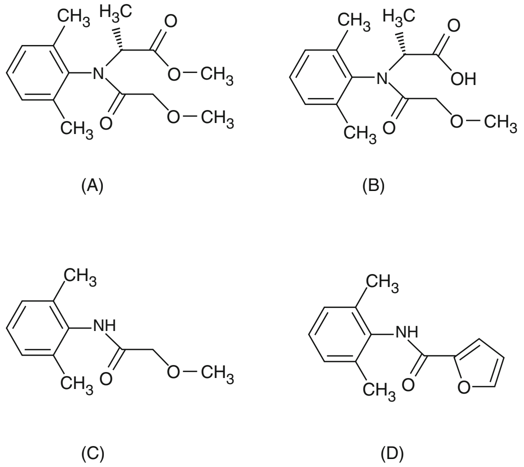


Fig. 20 Proposed MET metabolites in soil microorganisms

Buerge et al. (2003) observed correlations between soil pH and enantioselectivity of MET degradation. In alkaline soils MET half-life is in the range of 9–32 days, but in acidic soils it ranges between 16 and 127 days. It suggested a dependence of enantioselectivity degradation on soil pH. (−)-R-metalaxyl degraded is faster than (+)-S-metalaxyl (positive enantioselectivities) in acidic soils, but in alkaline soils an inverse situation is observed: S-enantiomer is degraded faster than R-enantiomer (negative enantioselectivities). The concentrations of both enantiomers also decrease according to first-order kinetics.

7.3 Toxicity of Metalaxyl

As mentioned above, MET is a chiral fungicide due to the presence of the stereogenic center in the alkyl moiety. The anti-fungicidal activity mostly originates from the R-enantiomer, which is also much more toxic than rac-metalaxyl (Chen and Liu 2008; Xu et al. 2011).

The research on the enantioselective distribution, degradation and excretion of MET after oral administration of rac-MET to mice was described in Zhang et al. (2014).

The concentration of R-MET was much higher than S-MET in heart, liver, lung, urine and feces. R-MET was also more persistent in the organism (degradation half-life: 3.0 h) then the S-MET (2.2 h). The main biotransformation reactions of MET were hydroxylation, demethylation and didemethylation. The concentration of products of these reaction was higher in urine and feces than those in tissues.

Above mentioned examples of different behavior of MET isomers indicate that the enantioselectivity of MET lies in distribution, degradation and excretion processes, which depend on the organism.

Metalaxyl-M causes cytotoxic and genotoxic effects on earthworms (*Eisenia fetida*). It caused an increase in the production of reactive oxygen species when the concentration was higher than 0.1 mg/kg of soil, which led to lipid peroxidation in earthworms. Metalaxyl-M can induce DNA damage in earthworms, and the level of DNA damage increased with increasing concentration of the fungicide. Metalaxyl-M also influences the activities of antioxidant enzymes, which results in irreversible oxidative damage in cells (Liu et al. 2014a, b).

MET is classified as Xn—harmful, N—dangerous for the environment (see Table 2), therefore, the attention of the researchers is focused rather on assessing the toxicity of the MET isomers (Chen and Liu 2008; Wilson et al. 2001; Yao et al. 2008; Kungolos et al. 2009; Xu et al. 2011; Bermúdez-Couso et al. 2013; Kalathoor et al. 2015), then their degradation products. However, to obtain complete knowledge about the influence of MET on the environment, the in-depth study on toxicity of its metabolites is necessary.

8 Influence of Pesticides and Their Degradation Products on Humans

Pesticides represent a potential threat to humans. Since pesticides are present in almost all parts of environment, the human exposure to agrochemicals can occur via a number of pathways such as indirect (e.g. through food, drinking water, residential and occupational exposure) and direct (oral, inhalation and dermal). However, the major concerns are from consumption of pesticide residues in food crops and contaminated water (Bakırcı et al. 2014). Therefore, to ensure the safety of food for consumers and to protect their health, the monitoring of pesticide residues in food products must be pursued. The levels of pesticide residues allowed in foodstuffs are legislatively controlled through setting maximum residue levels (MRLs). These MRLs limit the types and amount of pesticides that can be legally present on foods, as determined by various regulatory bodies which minimize consumer exposure to harmful or unnecessary intake of pesticides worldwide. The MRLs of pesticides residues in potatoes were established: 0.01 mg/kg for RIM, 0.02 mg/kg for LC, 0.05 mg/kg for MET, 0.2 mg/kg for DM, 0.3 mg/kg for TMX, according to European Union legislation (Commission Regulation 524/2011, 441/2012, 834/2013, 617/2014). Similar legislation applies in USA, China and other countries.

In European Union countries the concentration of pesticide residues in drinking water must not exceed the Maximum Allowable Concentration (MAC), that is established as 0.1 μg/L for a single pesticide and 0.5 μg/L for the sum of pesticides concentration (Council Directive 98/83/EC).

The specific risk is associated with contamination of water supplies that has a direct impact not only on human health and aquatic organisms, but also pesticides are translocated in the environment mainly with rainwater, which elutes them from the surface of plants and soil, and then they may be transferred with groundwater on long distances. Hereby, large areas are uncontrollably contaminated with agrochemicals.

It should be also added that the environment is contaminated not only by pesticides, but also by their degradation products. Therefore, the technologies that enable pesticide removal from water and soil purification are of great importance. There are many ways of water and soil purification, however many of these solutions have drawbacks. In fact, in some cases these procedures can leave the solution more toxic than it was originally (Lopes et al. 2008; Šojić et al. 2012; Mir et al. 2013; Zabar et al. 2012; Laberge and Rollinson 2013). As a result, aside from pesticide degradation products that are a result of chemical reactions that naturally occur in environment (hydrolysis, photolysis etc.), there are many water purification by-products.

Despite the growing awareness of the threat, which brings the usage of pesticides, replacement the old generation of pesticides with less toxic but more selective agrochemicals, or attempts to use "biopesticides", the pesticides are an inseparable part of modern agriculture.

The widespread use of pesticides causes, that these compounds are present in almost every element of the ecosystems. According to the latest studies (Bonmatin et al. 2015) the concentration of neonicotinoids, including TMX in soil is parts per billion (ppb)-parts per million (ppm) range; in water, parts per trillion (ppt)-ppb range, and plants, ppb-ppm range. According to (Starner and Goh 2012; Masiá et al. 2013; Van Dijk et al. 2013; de Lafontaine et al. 2014) the pesticides concentration in surface water has been found to exceed ecotoxicological limits imposed by national and international organizations. This provides multiple routes for chronic (and acute in some cases) exposure of non-target animals. More detailed information was presented by Main et al. (2014). Sediment and water samples (total 440) were collected before seeding, during the growing season and after the harvest of crops. At least one of the following neonicotinoids: clothianidin, thiamethoxam, imidacloprid, or acetamiprid was found in 16–91 % of the samples, depending on the time of sampling. TMX was predominant in water samples at mean concentration 40.3 ng/L; its maximum concentration was 1490 ng/L.

TMX was also determined in pollen or in pollen-derived matrices in the concentration range of 2.8–28.9 ng/g (Pohorecka et al. 2012; Stoner and Eitzer 2012; Sanchez-Bayo and Goka 2014). Depending on the source of material, TMX was determined in 1–37 % of collected samples.

Lafontaine et al. (2014) determined RIM in 24 % of surface water samples, collected in 2009–2011, at the concentration up to 233 ng/L. RIM exhibits low mammalian toxicity and short half-live in plants; therefore, its concentration in food of animal origin is often below MRL (Wu et al. 2012; Pang et al. 2016).

According to Allinson et al. (2015), MET was determined in 46 % of surface water samples at the concentration range 0.01–0.191 μg/L. MET was detected in 1 % of vegetables samples (total number of samples 300), in the concentration range: 0.019–0.034 mg/kg, thereby, the chronic and acute intake risk of this fungicide was assessed as low (Fang et al. 2016).

The monitoring studies conducted during the last 5 years revealed (Bakırcı et al. 2014; Sivaperumal et al. 2015; Szpyrka et al. 2015), that about 2–17 % of potatoes available on the European market contained MET.

Although the half-lives of pyrethroid pesticides in the environment are typically on the order of few days to weeks (Table 2), they are found in water, sediments, and biological samples (Chang et al. 2016; Corcellas et al. 2015). In 13 % of river water samples collected by Feo and coworkers (2010) DM was determined at the range of concentration 2–58.8 ng/L. These concentration levels were higher than median lethal concentration values found for DM when short time toxic effects were considered. At the same time 60 % of sediment samples contained LC at concentration of 0.42–16.6 mg/kg (Hunt et al. 2016). LC was determined in 21 % of peer samples at the concentration range 83–950 μg/kg (Han et al. 2015). DM was determined in 40 % of *Ginko biloba* samples (max. concentration 10.1 μg/kg) (Páleníková et al. 2015). LC and DM were determined in black, green and scented tea. The concentration of LC was in range 17.56–58.80 mg/kg. DM was determined in one black tea sample (2.31 mg/kg) (Cao et al. 2015).

According to above cited latest literature reports, pesticide residues are determined in less than 50 % of environmental samples, often below the maximum concentration set by legislation. Unfortunately, the studies rarely encompass also the monitoring of the pesticide degradation products, therefore the overall risk associated with pesticide residues in environment, and the corresponding human exposure, are difficult to assess.

Although, TMX has favorable safety profiles, due to its preferential affinity for nicotinic receptor (nAChR) subtypes in insects, poor penetration of the mammalian blood–brain barrier, and low application rates (Simon-Delso et al. 2015), there are more and more reports concerning its negative influence on mammals. All of these reports were summarized with critical comments by Sheets and coworkers (2015).

The results of the research on the enantioselective distribution and degradation of metalaxyl in different species of plants, invertebrates, and mammals, indicated that all these processes were enantioselective (Chen and Liu 2008; Xu et al. 2011; Li et al. 2013; Wang et al. 2014; Zhang et al. 2014). These results may have potential implications to predict toxicity and provide additional information associated with adverse health effects for risk assessment of MET.

Pyrethroids are extremely toxic to aquatic organisms (aquatic insects are sensitive to insecticide poisoning from less than 1 ppb concentrations) (Mugni et al. 2013; Antwi and Reddy 2015), but tend to be less toxic to mammals and birds than other types of insecticides, due to more effective and rapid biotransformation. However, pyrethroids are active in both insect, bird and mammalian neurons. Their potential to cause adverse effects in laboratory animals has been well studied in regulatory tests, and there are data which indicate that the neuronal effects do occur in humans. Exposure to DM leads to hepatotoxic, cardiovascular, immunosuppression nephrotoxic, neurotoxic and reproductive side effects for human and many species, including birds and fish (Bhaskar et al. 2012; Abdel-Daim et al. 2016; Doe et al. 2016).

9 Summary and Conclusion

Pesticides are essential in modern agriculture, however, their use is associated with toxicological risk. Therefore, for many years attention has been drawn to pesticide residue monitoring in the environment (soils, sediments, water, air, plant and animal tissues). Nevertheless, in many cases the information about pesticide concentrations in the environment is insufficient to assess the total risk connected with the presence of these compounds in environment. After spraying, agrochemicals undergo various transformations: they are degraded by microorganisms as well as they are decomposed in abiotic processes: hydrolysis, photolysis, redox-reactions etc. All of these processes are influenced by external (temperature, insolation, type of matrix etc.) and internal conditions (physico-chemical properties of the pesticide). As a result, a mixture of degradation products is formed. The ecotoxicological properties of pesticide by-products are usually different then the parent compounds. Therefore, it is essential to investigate the degradation pathways of pesticides and the influence of the degradation products on the environment.

For the review, we chose popular pesticides used in potato production. The potato is one of the most popular crops, and consequently, pesticides used in its cultivation are introduced into the environment in large quantities. While many studies focus on pesticide degradation processes, there are only few reports concerning degradation product toxicity.

Available results indicate both the significance (toxicity of degradation products to the investigated organisms) and the complexity of the problem (low levels of concentration, coexistence of many degradation products with a similar properties, difficulties in ensuring reproducibility of experimental conditions). A comprehensive research to determine overall pesticide impact on the environment is, however, yet to be undertaken.

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