

## Impact of fungicide and insecticide use on non-target aquatic organisms in rice paddy fields

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**ABSTRACT:** *The intensive use of plant protection products in rice paddy fields (*Oryza sativa* L.) has caused concern about the environmental impact on communities of non-target organisms that are natural inhabitants in these agroecosystems. The purpose of this review is to analyze the data currently available in the literature about some important fungicides and insecticides (such as trifloxystrobin, tebuconazole, tricyclazole, lambda-cyhalothrin, and thiamethoxam), which are currently used to control pests and diseases in rice paddy fields, as well as their effects on the community of non-target aquatic organisms.*

**Key words:** *plant protection products, benthic insects, *Oryza sativa* L., lowlands.*

## Impacto do uso de fungicidas e inseticidas sobre organismos aquáticos não alvos em lavouras de arroz irrigado

**RESUMO:** *O uso intensivo de produtos fitossanitários na lavoura de arroz irrigado (*Oryza sativa* L.) tem causado preocupação quanto ao impacto ambiental sobre comunidades de organismos aquáticos não alvos que são habitantes naturais nesses agroecossistemas. O objetivo da presente revisão é analisar os dados atualmente existentes na literatura sobre alguns importantes fungicidas e inseticidas (tais como trifloxistrobina, tebuconazol, triciclazol, lambda-cialotrina e tiametoxam), os quais são usados para controlar pragas e doenças na lavoura de arroz irrigado, bem como seus efeitos sobre a comunidade de organismos aquáticos não alvos.*

**Palavras-chave:** *produtos fitossanitários, insetos bentônicos, *Oryza sativa* L., terras baixas.*

## INTRODUCTION

Rice cultivation areas are considered humid agroecosystems, which are temporarily managed by man (LUPI et al., 2013). Such environments have a higher biological diversity of water and terrestrial invertebrates compared to other agricultural areas (STENERT et al., 2012). Although invertebrates are predominant in lowland environments where irrigated rice is grown, amphibians, fish, mammals, and aquatic plants can also be present in this agroecosystem.

Rice paddy field management practices cause changes in the community of non-target aquatic organisms. RIZO-PATRÓN et al. (2013) observed that invertebrates resistant to pollution were more abundant in conventional

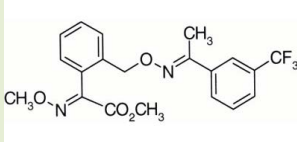
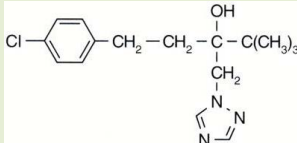
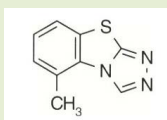
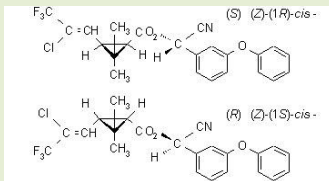
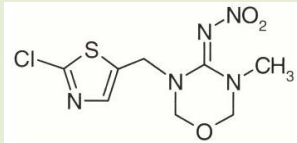
farming compared to organic farming and concluded that such organisms respond to both type of management and plant protection products applied to the crop.

The objective of this review was to analyze the literature data on some important fungicides and insecticides, which are currently used in the control of pests and diseases in rice paddy fields, and their effects on non-target community of aquatic organisms. The data presented below are from field and laboratory studies, which were conducted in Brazil and abroad.

### *Trifloxystrobin*

Trifloxystrobin (Table 1) is a mesostemic fungicide, which can be used as an active principle alone or in combination with other active principles.

Table 1 - Chemical and toxicological characteristics and application doses of plant protection products in rice paddy fields. Santa Maria, RS, 2015.

Active principles	Chemical groups	Structural formulas	$K_{ow}$ *	Toxicological classes	Doses (g a.i. ha <sup>-1</sup> )**
Trifloxystrobin	Strobilurin	251658240 	4.5	II	50
Tebuconazole	Triazole	251658240 	3.7	IV	100
Tricyclazole	Benzothiazole	251658240 	1.42	II	225
Lambda-cyhalothrin	Pyrethroid	251658240 	6.9	III	15.9
Thiamethoxam	Neonicotinoid	251658240 	-0.13	III	21.2

\* $K_{ow}$ : Octanol-water partition coefficient. \*\*a.i.: active ingredients. Source: ANVISA (2014), SOSBAI (2012).

In rice paddy fields, the trifloxystrobin + tebuconazole commercial formulation (which is used at a dosage of 50+100g of active ingredients (a.i.) ha<sup>-1</sup>, respectively) is used to control brown spot (*Bipolaris oryzae*), narrow brown leaf spot (*Cercospora janseana* = *C. oryzae*), and leaf scald (*Gerlachia oryzae* = *Rhynchosporium oryzae*) (SOSBAI, 2012).

In rice paddy fields, trifloxystrobin residues are highly correlated with ecological risk. However, how such processes occur is not yet clear. Trifloxystrobin showed a half-life in the range of 0.7-7.5 days in rice paddy fields. However, its major metabolite presented a high persistence in water, indicating that frequent application of the fungicide represent a long-term

potential risk for aquatic organisms that inhabit the rice agroecosystem (CAO et al., 2015).

Laboratory studies allowed to observe trifloxystrobin toxic effects on amphibians (JUNGES et al., 2012), crustaceans such as *Daphnia magna* (OCHOA-ACUNA et al., 2009) and *Hyaella azteca* (MORRISON et al., 2013), and fishes (USEPA, 2013). Fish may be present in rice fields by entering through the irrigation water or when they are added aiming rice-fish culture (LAWLER, 2001). Embryonic and larval development of the fish *Oryzias latipes* was changed after exposure to trifloxystrobin (ZHU et al., 2015a). LIU et al. (2013) reported that strobilurins, including trifloxystrobin, was toxic to *Ctenopharyngodon idella*, one of the most important fish species in Chinese aquaculture.

Trifloxystrobin also presented numerous toxic effects in embryos of *Gobiocypris rarus*, as observed through the increase in the number of malformations, changes in heart rate and enzyme activities, in addition to DNA damage, indicating that trifloxystrobin is highly toxic to fish embryos (ZHU et al., 2015b).

In chironomids, sediment chronic toxicity tests showed an  $CE_{50}$  (effective concentration for 50% of organisms) of  $450\mu\text{g L}^{-1}$  (28 d; *Chironomus riparius*) and NOEC (highest concentration in which effects are not observed) of  $200\mu\text{g L}^{-1}$  (28 d; *Chironomus riparius*). However, effects were less significant for metabolite CGA 321113, with an  $CE_{50}$  of  $49200\mu\text{g L}^{-1}$  (28 d; *Chironomus riparius*) and NOEC of  $25000\mu\text{g L}^{-1}$  (28 d; *Chironomus riparius*) (EUROPEAN COMMISSION, 2003). Studies conducted with the amphipod *Hyaella azteca* showed that trifloxystrobin toxicity may vary according to the environmental conditions; i.e., the presence of sediment may cause a decrease in toxicity of certain fungicide formulations (MORRISON et al., 2013).

#### Tebuconazole

Literature presents several laboratory studies on the effects of tebuconazole on parameters such as mortality, growth, behavior, and physiology of non-target aquatic organisms. A large part of these studies were conducted with crustaceans such as *Gammarus pulex* (ADAM et al., 2009), *Daphnia magna*, and *Americamysis bahia* (USEPA, 2013), fish such as *Rhamdia quelen* (KREUTZ et al., 2008), *Danio rerio* (ANDREU-SANCHEZ et al., 2012), *Cyprinodon variegatus*, and *Oncorhynchus mykiss* (USEPA, 2013), and mollusks such as *Crassostrea virginica* (USEPA, 2013). However, field studies testing the effects of active principles in the recommended doses were not reported in the literature.

The stress response in jundiá fingerlings of the species *Rhamdia quelen* was evaluated after acute exposure to plant protection products including tebuconazole fungicide. It was noticed that the presence of the stressful stimulus influenced the fish performance parameters more significantly than their own exposure to the fungicide (KOAKOSKI et al., 2014). Another recent study evaluated the tebuconazole toxic effects on various parameters of individuals of the species *Daphnia magna*. Results showed that the number of newborns per female was the highest sensitive parameter to tebuconazole exposure, and a seven-day recovery period in a toxicity-free medium was not enough to restore the reproduction normal parameters in daphnids pre-exposed to the fungicide (SANCHO et al., 2016). Tebuconazole toxic effects were observed

when amphipods of the species *Gammarus pulex* were fed with leaves exposed to tebuconazole fungicide, which caused a reduction in the organisms' feed rate (DIMITROV et al., 2014).

Enantio selectivity can contribute to the toxicity of plant protection products in the natural environment, and this phenomenon has been recently studied. Tebuconazole enantio selectivity was evaluated in three aquatic species (*Scenedesmus obliquus*, *Daphnia magna*, and *Danio rerio*) and R - (-) - tebuconazole was about 1.4 - 5.9 times more toxic than S - (+) - tebuconazole. Tebuconazole enantio selectivity showed a significant correlation with soil properties. This property may be a common phenomenon in the biodegradation of chiral triazole fungicides and aquatic toxicity, and should; therefore, be considered when the ecotoxicological risks of these compounds in the environment are assessed (LI et al., 2015). Currently, methods to determine tebuconazole enantio selectivity have been studied (LIU et al., 2015). A recent study showed that no significant enantio selective degradation of tebuconazole was observed in sterile conditions (ZHANG et al., 2015), indicating that organic matter is important in fungicide enantio selective degradation.

When plant protection products are released into the environment, highly toxic processing products can be generated. However, the occurrence of these products and their potential environmental risk are difficult to predict. Transformation products of the fungicide tebuconazole were identified in the soil during a field study, which detected 22 known and 12 still unknown transformation products (STORCK et al., 2016). This suggested that further studies on derivatives toxicity to non-target aquatic organisms after degradation of this fungicide in the environment are important.

In addition to the toxic effects on physiological functions of organisms, the effects on DNA are also important when the environmental risk to non-target organisms is considered. The genotoxic potential of active principle tebuconazole was assessed in snail embryos of the species *Cantareus aspersus*, in which individual changes were observed with tebuconazole doses starting from  $50\mu\text{g L}^{-1}$  (BAURAND et al., 2015).

#### Tricyclazole

Tricyclazole, which is a systemic fungicide of the benzothiazole chemical group, is applied at a dose of  $225\text{g a.i. ha}^{-1}$  in rice cultivation to control rice blast (*Pyricularia grisea*) (SOSBAI, 2012). Studies indicated that tricyclazole presents a high risk of environmental contamination, is not readily hydrolysable in the environment, and has a high capacity for soil adsorption (PADOVANI et al., 2006).

Although tricyclazole is one of the fungicides most used in rice paddy fields, there is still little information in the literature about its toxic effects on non-target aquatic organisms, and the information available refers to acute toxicity tests with bioindicators (in a few species however) in laboratory conditions. Amphibian mortality, after exposure of *Rana limnocharis* to tricyclazole, was observed by PAN & LIANG (1993), who determined a  $CL_{50}$  of  $19425\mu\text{g L}^{-1}$ . The  $CL_{50}$  values were determined for the fish *Lepomis macrochirus* ( $2460 (1609-3880)\mu\text{g L}^{-1}$ ) and *Oncorhynchus mykiss* ( $1801 (1500-2200)\mu\text{g L}^{-1}$ ) (USEPA, 2013). Intoxication of mollusk *Crassostrea virginica* embryos was also determined in laboratory conditions ( $CE_{50} = 32000\mu\text{g L}^{-1}$ ) (USEPA, 2013).

Tricyclazole caused an increase in the triglyceride, cholesterol, glucose, and lactate levels in fish of the species *Danio rerio*, in addition to enzymatic disorders observed after the organisms were recovered at the end of the experiment (SANCHO et al., 2009). One of the few studies about the effects of tricyclazole on benthic macroinvertebrates was developed by ROSSARO & CORTESI (2013), who did not find significant negative effects of the fungicide in field tests. In tests for acute toxicity under laboratory conditions, tricyclazole also showed a low toxicity ( $CL_{50 (48\text{ h})} = 26000\mu\text{g L}^{-1}$ ) on invertebrates.

#### Lambda-cyhalothrin

Lambda-cyhalothrin, which is a halogenated pyrethroid insecticide, comprises two stereoisomers, being widely used in pest control (COLOMBO et al., 2013). It is used in rice paddy fields to control small rice stink bug (*Oebalus poecilus*), in combination with insecticides of the neonicotinoids chemical group such as thiamethoxam ( $15.9$  and  $21.2\text{g a.i. ha}^{-1}$ , respectively) (SOSBAI, 2012). Pyrethroid insecticides, such as lambda-cyhalothrin, are hydrophobic compounds that, in aquatic environments, can bind to organic matter (e.g., debris, leaves, and phytoplankton), which are important in the benthic macroinvertebrate community structure. However, pyrethroid coefficient of partition between different fractions of organic carbon depends on the bioavailability, which may influence toxicity to aquatic invertebrates (MAUL et al., 2008).

In nature, there is a range of contaminants that interact with each other, causing synergistic or antagonistic effects on species. Lambda-cyhalothrin, cadmium, and the neonicotinoid imidacloprid were tested in combination, and their toxic effects on earthworms of the species *Eisenia fetida* were analyzed. The combination of lambda-cyhalothrin and cadmium resulted in light synergistic effects on organisms; whereas,

binary mixtures with imidacloprid resulted in antagonistic effects, which were more significant in ternary mixtures with this insecticide (WANG et al., 2015).

In laboratory tests, SCHROER et al. (2004) observed that *Chaoborus obscuripes* (Diptera: *Chaoboridae*) was the species most sensitive to lambda-cyhalothrin ( $CE_{50 (48\text{ and }96\text{ h})} = 0.0028\mu\text{g L}^{-1}$ ), followed by other insect larvae of the orders Hemiptera and Ephemeroptera and macrocrustaceans, which were relatively sensitive ( $CE_{50 (48\text{ and }96\text{ h})} = 0.01-0.1\mu\text{g L}^{-1}$ ). The groups of microcrustaceans (Cladocera, Copepoda) and insect larvae of the orders Odonata and Chironomidae were the least sensitive ( $CE_{50 (48\text{ h})} > 0.1\mu\text{g L}^{-1}$ ).

Several recent studies on the toxic effects of lambda-cyhalothrin in fish can be reported in the literature. The quality of sperm from individuals of the species *Oncorhynchus mykiss* (rainbow trout) was significantly reduced by exposure to lambda-cyhalothrin (KUTLUYER et al., 2015). In fish *Danio rerio*, lambda-cyhalothrin caused disturbance in the endocrine system, and the T3 and T4 hormones were significantly altered after exposure to the insecticide (TU et al., 2016). In another study conducted with zebrafish embryos, it was observed that synthetic pyrethroids have a high bioconcentration capacity, suggesting that pyrethroids have a highly-cumulative risk for fish (TU et al., 2014).

Recent studies showed that enantio selectivity may be another factor to be considered in the toxicity of chemicals in the environment. Bioavailability and enantio selectivity of lambda-cyhalothrin and bifenthrin was observed in earthworms of the species *Eisenia fetida*. Results showed that lambda-cyhalothrin was more easily adsorbed on the soil than bifenthrin, and bioaccumulation of both products was enantio selective (CHANG et al., 2016). Recently, WIELOGÓRSKA et al. (2015) observed that pyrethroid metabolites are concerning regarding their estrogenic activity, which is relatively higher than their parent compounds.

#### Thiamethoxam

Neonicotinoids are highly potent and selective systemic insecticides (VEHOVSZKY et al., 2015). They are persistent in the environment, exhibit high bleaching capacity, and are highly toxic to many species of invertebrates (MORRISSEY et al., 2015). Temporary wet areas, as is the case of rice paddy fields, are among the places of greatest risk for contamination by neonicotinoids (MAIN et al., 2016).

Imidacloprid is the neonicotinoid most studied up to now, representing 66% of the 214 toxicity tests with neonicotinoids reported in the literature. Insects belonging to the orders Ephemeroptera, Trichoptera, and Diptera appear to be the most sensitive

among the species evaluated, whereas crustaceans in general are less sensitive (MORRISSEY et al., 2015). Aquatic insects are particularly vulnerable to neonicotinoids. However, there are few studies on the biological effects of thiamethoxam in fish, amphibians, and mollusks (ANDERSON et al., 2015). Recent studies showed the toxic effects of thiamethoxam in crustaceans (*Gammarus kischineffensis*) (UĞURLU et al., 2015; DEMIRCI et al., 2015), *Daphnia magna* and *Americamysis bahia* (USEPA, 2013), fish of the species *Channa punctata* (KUMAR et al., 2010), *Cyprinodon variegatus*, *Lepomis macrochirus*, and *Oncorhynchus mykiss* and mollusks of the species *Crassostrea virginica* (USEPA, 2013). BARBEE & STOUT (2009) determined  $CL_{50}$  values for *Procambarus clarkia* ( $967 (879-1045)\mu\text{g L}^{-1}; 96\text{h}$ ) under laboratory conditions, and insects of the genus *Chironomus* sp. presented  $CL_{50 (48\text{h})} = 35 (33-38)\mu\text{g L}^{-1}$  (USEPA, 2013). VEHOVSZKY et al. (2015) observed that neonicotinoids inhibited the cholinergic neurotransmission in the nervous system of mollusks of the species *Lymnaea stagnalis*. The authors emphasized that aquatic animals, including mollusks, are in direct contact with the contaminants present in the aquatic environment, and they can thus be a suitable model for future studies on the neuronal and behavioral consequences of neonicotinoid poisoning.

In a recent study, BREDESON et al. (2015) found clothianidin, a toxic metabolite of thiamethoxam, in aphids that were fed with wheat plants treated with thiamethoxam. This suggested that studies on the effects in herbivores of thiamethoxam residues and its metabolites are important. TAILLEBOIS et al. (2014) described the synthesis of two new fluorescent thiamethoxam derivatives and compared their toxicities on the aphid *Acyrtosiphon pisum*. Results showed that these compounds presented toxic effects, acting as agonists on insect nicotinic acetylcholine receptors.

## CONCLUSION

The literature showed that the plant protection products presented here have the potential to cause negative effects on non-target aquatic organisms inhabiting rice paddy fields. Triazoles and benzothiazoles persist in the environment and may cause a negative impact on communities of non-target aquatic organisms. Strobilurins, such as trifloxystrobin, have a low persistence in the environment, although they are toxic to aquatic organisms. Pyrethroids are hydrophobic compounds that can bind to the soil organic matter. They are among the most studied chemical groups, being highly toxic to aquatic organisms. Currently, special attention has been given to neonicotinoids, as this class

of insecticides has many active principles and their risks to non-target organisms are little known. However, they persist in the environment and have a high capacity to leach and contaminate water bodies, impacting the biological communities that inhabit these ecosystems.

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