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Laboratory and field dissipation of penoxsulam, tricyclazole and profoxydim in rice paddy systems

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HIGHLIGHTS

- ▶ Environmental fate and dissipation study, of main rice pesticides, in paddy water and soil.
- ▶ Laboratory and 2-year field studies of penoxsulam, profoxydim and tricyclazole.
- ▶ Fast dissipation of profoxydim in paddy water and soil.
- ▶ Tricyclazole was the most persistant pesticide, especially in paddy soil.
- ▶ Potential risk for contamination of natural water resources near paddy fields.

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ABSTRACT

Rice cultivation relies on pesticide applications to ensure high yields. However, the regular use of pesticides seriously affects the quality of neighboring surface water systems. Thus complete knowledge of the environmental fate and dissipation of pesticides in the paddy rice environment should become available. So far only a few studies have provided comprehensive assessment of the dissipation of pesticides under the submerged cultivation conditions followed in rice. Thus, laboratory and 2-year field studies were performed to assess the dissipation of two new generation rice herbicides (penoxsulam and profoxydim) and one of the most important rice fungicides (tricyclazole). A good agreement between laboratory and field experiments was observed with a faster dissipation of penoxsulam and tricyclazole under field conditions. Profoxydim was the least persistent chemical (DT_{50} soil < 1d; DT_{50} water 0.5–1.2 d), followed by penoxsulam which persisted for longer particularly in the water compartment ($DT_{50water}$ = 3.8–5.9 d). Tricyclazole was the most persistent pesticide, especially in the soil compartment with DT_{50} values of 44.5–84.6 (field) and 197 d (laboratory). These results could be utilized for the assessment of the environmental risk associated with the use of those pesticides in rice cultivation and the determination of potential mitigation measures for minimizing the risk for contamination of neighboring natural water resources.

1. Introduction

Rice is considered a high-value crop mainly cultivated in south Europe under submerged conditions. Weed and fungal infestations significantly diminish rice yields and regular applications of pesticides are required for their control. However, the high pesticide loads used in rice cultivation have been found to have a serious impact on the quality of neighboring natural water resources which constitute unique ecosystems hosting birds, mammals and aquatic organisms. Indeed previous monitoring studies conducted in rice-cultivated basins in Spain (Tarazona et al., 2003), Italy (Capri et al., 1999), Portugal (Silva et al., 2006) and Greece (Papadopoulou-Mourkidou et al., 2004) have detected high concentrations of rice pesticides. Considering the unique cultivation conditions of rice, it is important to determine the persistence and fate of pesticides used in rice cultivation in order to predict with high certainty the risk for contamination of natural water resources by these pesticides.

Since the withdrawal of propanil and the limited use of molinate, weed control in rice fields in Europe relies mostly on a limited number of chemicals including penoxsulam and profoxydim. Penoxsulam [*3-(2,2-difluoroethoxy)-N-(5,8-dimethoxy[1,2,4]triazolo[1,5-c] pyrimidin-2-yl)-α,α,α-trifluorotoluene-2sulfonamide*] is a sulfonamide

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herbicide which is used for the post-emergence control of annual grasses, sedges and broadleaf weeds in rice cultivation (Roberts et al., 2003). It inhibits acetolactate synthase, a prime enzyme in the biosynthesis of brached-amino acids. A limited number of studies have investigated its persistence in the paddy environment. It has been found that in laboratory conditions penoxsulam is dissipated rapidly in paddy water with photo-degradation being the most important process (Jabusch and Tjeerdema, 2006a) and relatively rapidly in paddy soil with microbial degradation being the dominant process (Jabusch and Tjeerdema, 2006b). Additionally it is weakly adsorbed on soil according to Jabusch and Tjeerdema (2005). Field studies verified the low persistence of penoxsulam with DT_{50} values ranging from 3.1 to 7.1 d (Roberts et al., 2003). A more recent study reported DT_{50} values of 1.28–1.96 and 20.2–27.7 d in paddy water and paddy soil respectively (Kogan et al., 2012). Penoxsulam is considered particularly toxic to aquatic plants with EC_{50} of 0.086 mg L^{-1} for *Pseudokirchneriella subcapitata* and 0.0033 mg L^{-1} for *Lemna gibba* (EFSA, 2009). Thus, despite its short persistence, its presence even at low concentration in surface waters entails an unacceptable risk for aquatic plants. Therefore, the environmental fate of penoxsulam in paddy systems which are the sinks for environmental contamination should be studied.

Profoxydim [*5RS)-2-{(EZ)-1-[(2RS)-2-(4-chlorophenoxy) propoxyimino] butyl}-3-hydroxy-5-[(3RS)-thian-3-yl]cyclohex-2-en-1-one*] is a herbicide used in rice cultivation for the post-emergence control of the grass-weed *Echinochloa crussgalli*. Similarly to penoxsulam, it acts by inhibiting the biosynthesis of branced amino acids (Ruiz-Santaella et al., 2003). Little is known regarding its environmental fate in the paddy environment. Sanchez et al. (2006) observed a rapid dissipation of profoxydim in paddy water and soil. More recent regulatory studies reported that profoxydim is not persistent in the paddy environment and shows a moderate to low adsorption affinity which is highly dependent on pH (EC, 2011).

Rice cultivation suffers from severe infestations by *Pyricularia oryzae* which is the causal agent of rice blast (Webster and Gunnell, 2000). Tricyclazole [*5-methyl-1,2,4-triazolo[3,4-b]benzothiazole*] is extensively used for its control. However, its regular use has resulted in contamination of natural water resources in rice cultivated areas (Tanabe et al., 2001; Padovani et al., 2006). A few studies have investigated the environmental fate of tricyclazole in rice paddies. Tricyclazole is dissipated relatively fast in paddy water with DT_{50} values ranging from 2.1 (Phong et al., 2009a) to 11.8 d (Phong et al., 2009b). In contrast, tricyclazole is stable in the soil environment with DT_{50} values of 203–407 d (Phong et al., 2009b) or 97–913 d (Fernandes et al., 2006). Recently, tricyclazole has not been included in Annex I to Council Directive 91/414/EEC due to toxicity and health concerns, and therefore the withdrawal of authorisations for plant protection products containing that substance is needed (EC, 2008).

Overall, there are limited informations concerning the environmental fate of pesticides in rice cultivation and more comprehensive studies are needed to accurately predict the environmental risk entailing their use. The objective of this study was to investigate the dissipation of three common rice pesticides, penoxsulam, profoxydim and tricyclazole in all relevant environmental compartment of the rice ecosystem at both laboratory and field scale. In addition, the potential of plant uptake and accumulation of pesticide residues in the rice grains was also explored.

2. Materials and methods

2.1. Chemicals

HPLC gradient grade acetonitrile and water were supplied from Merck (Darmstadt, Germany). Analytical standards of the studied pesticides were used for analytical purposes. Tricyclazole (99.0%) and profoxydim (lithium salt, 99.2%) were supplied from Riedel-de Haen (Seelze, Germany) while penoxsulam (99.1%) was donated by DowAgrosciences (Indianapolis, USA).

2.2. Laboratory experiment

The dissipation of penoxsulam, tricyclazole and profoxydim was investigated in rice microcosms where flooded conditions were simulated. Relevant physicochemical properties of the pesticides studied are given in Table 1.

The soil used was collected from a paddy field from the research station of the Cereal Institute of Thessaloniki, a member of the National Agricultural Research Foundation of Greece, Kalochori, Thessaloniki (latitude 40°37′0.64″N, longitude 22°49′49.99″E). Prior to its use the soil was partially air-dried and sieved (2 mm sieve). The soil was characterized as silty loam (sand 38%, silt 38%, clay 24%) with pH 7.78, electrical conductivity 920 μS cm^{-1} and organic carbon content of 2.35%.

Rice microcosms consisted of glass jars (500 mL) where 150 g of soil were added to form a soil layer of 5 cm. The soil in the flasks was then flooded with 250 mL of deionized water to form a water layer of approximately 10 cm. After their preparation, the microcosms were left to equilibrate for a week prior to pesticide application.

Herbicides penoxsulam and profoxydim were applied as aqueous solutions of their commercial formulations (penoxsulam; VIPER® 2.04% and profoxydim; AURA® 20%). Before their application, the water from the microcosms was carefully removed and herbicides were applied directly onto the soil. Herbicides were applied at their recommended dose for weed control (penoxsulam 2 L ha^{-1} corresponding to 0.07 mg kg^{-1} soil dry weight; profoxydim 1 L ha^{-1} corresponding to 0.33 mg kg^{-1} soil dry weight). Approximately 48 h later, the soil in the microcoms was flooded (250 mL water) to simulate the proposed mode of application for the two herbicides. In contrast, tricyclazole was directly applied as aqueous solution of the commercial formulation (BEAM®, 75%) onto flooded microcosms according to Good Agricultural Practice (GAP) guidelines. Tricyclazole was applied at the recommended dose (600 g ha^{-1}) for fungal control. After their preparation, all microcosms were incubated at standard conditions of 30–33 °C and 75% relative humidity which are close to the climatic conditions prevailing during rice cultivation in south Europe. Triplicate soil microcosms for each pesticide were removed from the incubator at regular intervals after pesticide application and used for pesticide residue analysis in water and soil as is described below. The overlaying water of the microcosm was carefully removed with a pipette, excess water was carefully drained and the remaining soil was collected and stored.

2.3. Field experiment

The dissipation of penoxsulam, profoxydim and tricyclazole was also determined in the field for two consecutive years (2007–2008). A block design with triplicate rice plots (60 × 70 × 50 cm, each containing *ca.* 250 kg soil) for each of the studied pesticides was followed (Fig. 1). A japonica type cultivar called ‘‘DIMITRA’’ was planted in the rice plots in the middle of May.

Pesticides were applied with a portable field plot sprayer with compressed air (Azo-Sprayers, Bjede, The Netherlands) with 6 AJ Teejet AI-110015 nozzles (Teejet spray system Co., Wheaton, USA), with 300 L ha^{-1} water volume and pressure at 2.8 atm. A flat partition (1 m × 1 m) was used, between the plots, as to avoid spraying contamination.