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Review

Ecological risk analysis of pesticides used on irrigated rice crops in southern Brazil

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HIGHLIGHTS

- Bentazon and Carbofuran were observed in the Brazilian irrigated rice crop water.
- Environmental Bentazon residues was 37 times lower than the smallest EC_{50}/LC_{50} value.
- Carbofuran presented deterministic risk but without any associated probability.

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ABSTRACT

Based on studies conducted in the past decade in the southern region of Brazil to determine residue levels of the pesticides normally used on irrigated rice crops, changes can be observed in relation to the presence of pesticides in the waters of the main river basins in Santa Catarina State. In previous harvests, the presence of residues of 7 pesticides was determined, with the herbicide bentazon and the insecticide carbofuran being the products showing highest frequency. Following toxicological tests conducted with 8 different test organisms, deterministic and probabilistic risk analysis was performed to assess the situation of the river basins in areas used for the production of irrigated rice. Of the species tested, the herbicide bentazon showed greatest toxicity toward plants, but did not present an ecological risk because in the worst-case scenario the highest concentration of this pesticide in the environment is 37 times lower than the lowest EC_{50}/LC_{50} value obtained in the tests. The insecticide carbofuran, which had the highest toxicity toward the organisms used in the tests, presented an ecological risk in the deterministic analysis, but without any associated probability. The results highlight the need for increased efforts in training farmers in crop management practices and for the continual monitor of water bodies for the presence of pesticide residues.

Contents

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1. Introduction

The southern region of Brazil produces 60% of the rice grown in the country. The cultivation techniques used in this region are the pre-germinated (irrigated soil) system and sowing in dry soil with irrigation by flooding, which is performed after weed control (Eberhardt et al., 2012). The areas planted with irrigated rice are intensively farmed, i.e. without rotation, due to difficulties associated with using these areas for other activities. This intensive use favors the emergence and proliferation of pests, weeds and diseases, leading to the need for the application of pesticides to ensure the profitability of the crop. Many of these chemical inputs (fertilizers, herbicides, insecticides and fungicides) are applied directly to the water layer or sprayed onto the plants from which they can reach the water, resulting in the transport of residues to areas outside the fields if the application is not managed in the recommended way (Noldin et al., 2012). The risk of pesticides being carried from the crops to surface water and groundwater resources poses a threat to water quality in irrigated rice production regions (Silva et al., 2009).

Following a study carried out on the major river basins in Santa Catarina State, (southern region of Brazil), for the rice harvests of 1998/1999 and 1999/2000 (Resgalla et al., 2007), a program was implemented, starting in the 2006/2007 harvest, to monitor pesticide residues in water bodies in the area around the crops. Twenty-one products (Table 1) widely used by farmers were analyzed, and the presence of the residues of seven pesticides was found: the herbicide bentazon and the insecticide carbofuran being the products with the highest rate of occurrence and concentration (Table 2) (Deschamps et al., 2013; Noldin et al., 2015). In comparison with the 1998/1999 and 1999/2000 harvests (Resgalla et al., 2007), the herbicide quinclorac presented a reduced occurrence in the river basins studied.

To assess the risk to water resources posed by the pesticides used in irrigated rice cultivation, the toxicity of the herbicide bentazon and the insecticide carbofuran toward different test organisms was investigated. This allowed an ecological risk analysis to be performed, which can serve as a basis for contamination mitigation projects in areas planted with irrigated rice crops.

2. Material and methods

During the harvests of 2006/07, 2009/10, 2010/11 and 2013/14, 498 water samples were collected from rivers in five river basins located in Santa Catarina State, in the southern region of Brazil, which eventually flow into the Atlantic Ocean (Fig. 1). The monitoring carried out in these basins showed that, of the 21 products investigated, the herbicide bentazon and the insecticide carbofuran had the highest occurrence in the waters of these rivers (Table 3). Bentazon was found in all five basins studied, while carbofuran was found in four of the five basins studied.

2.1. Bentazon and carbofuran residues

The residues of the herbicide bentazon and the insecticide carbofuran were determined by High Performance liquid chromatography (HPLC - Shimadzu LC10ADVp with UV-detector SPD10A Vp) having been isolated by solid phase extraction (SPE-C18, 3 mL, 500 mg Phenomenex/Strata), with an extracted sample volume of 300 mL. To analyze bentazon, the sample was acidified to pH 2.0 with HCl and eluted with 5 mL of acetonitrile and 4 mL of ethyl acetate. The recovery volume was dried at 45 °C and dissolved in mobile phase. The volume injected was 20 μL, using 245 nm to quantify the product and confirmed by 270 nm. The column was a Shimpack C18, 5 μm particle size, 250 × 4.6 mm and mobile phase starting 30:70 acetonitrile: water acidified to pH 2.0 with acetic acid, flow 0.5 mL min^{-1}, reaching 55:45 in 10 min. Under these conditions, the retention time was 23 min. For carbofuran, acidification of the sample is not needed, and for the elution 9 mL of acetonitrile is used, dried and dissolved in mobile phase acetonitrile:water (50:50). A Phenomenex/Luna C18 (150 × 4.6 mm 3 μm particle) column was used, with flow of 0.4 mL min^{-1} and 75:25 gradient in 10 min. The retention time of carbofuran was 11.4 min, with UV detector setted in 225 nm to quantification and confirmed by 245 nm. For both pesticides, the quantification limit was less than 0.1 μg L^{-1} with recovery higher than 90%, and variations according to the brand of SPE chosen.

2.2. Toxicity tests

The bentazon and carbofuran toxicity tests were carried out based on the concentrations of the active ingredients of each commercial formulation, preparing stock solutions of 1 g L^{-1}. For bentazon the product Basagran 600 was used in the tests and for carbofuran the product Furadan 100G was used. For each test organism the test solutions were prepared based on a literature search or on preliminary tests.

The toxicological tests were carried out using five test organisms: the phytoplankton species *Pseudokirchneriella subcaptata*, *Scenedesmus subspicatus* and *Skeletonema costatum*, the sea urchin *Lytechinus variegatus* and the marine microcrustacean *Mysidopsis juniae*. These species were selected for their standardization in test

Table 1
Main agrochemicals analyzed in studies to monitor residues in areas of irrigated rice crops in the state of Santa Catarina (according to Deschamps et al., 2013; Noldin et al., 2015).

Herbicides			Insecticides	Fungicide
Bentazon	Imazapic	Thiobencarb	Carbofuran	Tricyclazole
Quinclorac	Penoxsulan	Fenoxaprop	Fipronil	
2,4 D	Pyrazulfuron Ethyl	Oxyfluorfen		
Nominee	Simazina	Oxadiazon		
Cyclosulfamuron	Atrazina	Molinate		
Imazethapyr	Propanil	Metsulfuron Methyl		