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Distribution and Persistence of Tricyaclazole in Agricultural Field Soils

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Abstract Soil is the major sink for majority of pesticides applied on agricultural crops and its fate depends on variety of factors. There is little research on fate of pesticide in field soil under different climatic conditions and there is a need of study on the influence of climate on pesticide degradation and persistence in soil. In the present study, the persistence and distribution of tricyclazole was investigated in rice field soil under the influence of cold winter condition. Field experiment was carried at 35 different field sites from 6 provinces in Republic of Korea. Limit of detection and limit of quantification of tricyclazole were found to be 0.005 and 0.0165 mg/kg, respectively. The concentrations of tricyclazole in soil samples ranged from 0.387 mg/kg in sites in Gyeongsangbuk-do areas and lowest 0.021 mg/kg in sites from Chuncheongnam-do areas. In natural environmental conditions, tricyclazole persisted longer than 11 months post application in agricultural field soils. Our result indicates the influence of cold climatic condition on the persistence of tricyclazole.

Keywords Tricyclazole · Distribution · Persistence · Agricultural soil · Cold climatic condition

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Korea is one of the major rice-producing countries in Asia, and at present is capable of producing enough rice for self-sufficiency. The increase in rice production to meet the food demand has led to massive and indiscriminate use of pesticides in rice paddy fields, with application of approximately 10.70 kg of active ingredients per hectare in Korea (Barker et al. 1985). Although intensive applied pesticides in rice paddy fields have increased grain production, its use has several drawbacks. Due to indiscriminate use of pesticides, residues of several pesticides can be found in rice, not only affecting the quality of rice but also threatening human health and the environment (Demont et al. 2008; WHO 2005).

Tricyclazole (5-methyl-1,2,4-triazolo(3,4-b) benzothiazole) is the most commonly used fungicide applied for controlling the rice blast disease in Asian countries. It provides rice with long-term protection during the whole growth process because of its stability and accumulation in soil (Padovani et al. 2006). Because it is relatively stable in water-soil systems the potential environmental risk of tricyclazole is considered significant (Padovani et al. 2006). The WHO has classified tricyclazole as a moderately hazardous pesticide (WHO 2005). Its toxicity for mammals is low however, its toxicity for aquatic organisms is considerable (rainbow trout and goldfish fingerlings LC_{50}, 96 h are 7.3 and 13.5 mg/L, and for Daphnia, 48 h is >20 mg/L) (Tomlin 2003).

Tricyclazole runoff from paddy fields is responsible for the contamination of river and ground water (Tanabe et al. 2001; Ebise and Inoue 2002; Nakano et al. 2004). The environmental risk of this compound is considered high for surface water (Padovani et al. 2006). However, the

environment fate assessment of this pesticide in soil is scarce. Laboratory studies indicate that it is quite persistent in soil (21–913 days) depending on soil types (Padovani et al. 2006; Liu et al. 2008; Fernandes et al. 2006; Vogue et al. 1994), however, its persistence in real environmental field condition is unknown.

The fate of pesticides in the soils are affected by the nature of the pesticide, the soil type, cover crops, soil cultivation, the mode of application of the pesticide to the soil, and pesticide formulation. Climatic factors temperature, sunlight, soil microorganisms and soil moisture, facilitate pesticide degradation and persistence. Studies dealing with the effect of temperature on soil microbial biomass (Insam et al. 1989), soil microbial activity (Insam 1990) and pesticide degradation (Torstensson et al. 1989) demonstrate the important influence of the climatic factor. In this study, we report on the concentration levels, distribution patterns and persistence of tricyclazole in rice paddy soil in real field under different climatic conditions.

Materials and Methods

The analytical standards of tricyclazole (99.8 %) used was purchased from Dr Ehrenstorfer GmbH (Augsburg, Germany). Sodium chloride and anhydrous sodium sulfate were obtained from Dae Jung (Korea). Dichloromethane, acetone, and acetonitrile were obtained from J. T. Berker (USA), and *n*-hexane from Kanto chemicals Co. Inc. (G.R. Japan). All the chemicals were of analytical grade. Stock standard solution (1,000 mg/L) of tricyclazole was prepared in acetonitrile. Working solutions were prepared by serial dilution of the stock solutions to obtain the concentrations 1.0, 0.5, 0.3, 0.2, 0.1, 0.05 and 0.01 mg/L using the same solvent. All the working standard solutions and stock solutions were maintained in amber bottles and stored at 4°C and at −20°C, respectively.

Samples were collected from 35 different agricultural farms from six provinces in Korea (Fig. 1). These agricultural farms are located in the southern part of Korea and are major rice growing areas in Korea. The first sampling was done after harvest in October–November (autumn, 2010) when most of the water used has been drained. The second sampling was done in March–April (spring, 2011) after 4 months of chilling cold winter. Winter season are bitterly cold and dry in Korea, temperature usually falling as low as −5°C. The upper 0–10 cm of agricultural field soil samples (approximately 1 kg) were separately collected from at least six different points in each sites, placed in labeled polyethylene bags and transported to the laboratory on the same day. The collected samples were air-dried in shady conditions and mixed homogeneously, and stored below 4°C until analysis. Soil samples were analyzed in triplicates.

Fifty gram samples were placed into Erlenmeyer flasks (300 mL) into which 100 mL of acetonitrile solution were added, and then the mixture was shaken for 30 min on a mechanical shaker (Jeio Tech IS-971R, Republic of Korea) at 300 rpm. The extracts were filtered through filter paper (Whatman No. 42) using a Buchner funnel under suction. The residue was then washed with another 50 mL of fresh acetonitrile and the combined filtrate was placed into a separatory funnel (500 mL) into which 50 mL of saturated NaCl (5 %) solution and 100 mL of distilled and deionized water were added. The mixture was then partitioned twice with dichloromethane (80 mL + 70 mL). The combined organic layer was dried over 20 g of anhydrous Na_2SO_4 followed by evaporation to dryness under vacuum at 40°C (Vacuum evaporator, Eyela, Japan). The extract was reconstituted in 5 mL of acetone/*n*-hexane (20/80) and subjected to clean-up. The reconstituted samples were evaporated and re-dissolved in 3 mL of methanol/dichloromethane (30/70). The samples were loaded into an SPE-NH_2 cartridge (1 g) (55 mesh, Phenomenx, USA) which were conditioned with 5 mL of dichloromethane. The columns were washed by methanol/dichloromethane (5 mL) and tricyclazole was eluted with 5 mL of methanol/dichloromethane. The elutes were evaporated at 40°C, reconstituted with 2 mL of acetonitrile, and subjected to instrumental analysis.

Agilent 1200 HPLC system equipped with a Hitachi L-6200 pump, a Luna C18 analytical column (250 cm × 4.5 mm (i.d.), 5 μm, Phenomenex Luna) was used for tricyclazole analysis. The UV detector was set at 254 nm. The mobile phase system was 0–5 min 3 % water/acetronitirle (70/30, v/v) pumped at flow rate of 1.2 mL/min. The injection volume was 10 μl. In order to avoid a false positive result, all positive and ambiguous results from HPLC analysis were further confirmed by HPLC/MSD.

Results and Discussion

The linearity value calculated as determination coefficients (r^2) was always 0.999. The mean recovery determined by fortifying soil samples with tricyclazole at two different spiking levels (0.05 and 1.0 mg/kg) was found to be 98 % with relative standard deviation (RSD) below 6 %. LOD and LOQ of tricyclazole were found to be 0.005 and 0.0165 mg/kg, respectively. The spatial distributions and concentration of residue levels of tricyaclazole in the soil samples are shown in Fig. 1. All the 35 sites studied in the present study had low levels of tricyclazole residues. In general, the average concentration of tricyclazole residues in agricultural fields from Jeollabuk-do, Gyeongsangnam-do, Chuncheongnam-do, Chuncheongbuk-do, jeollanam-do, and Gyeongsangbuk-do averaged to 0.067, 0.134,

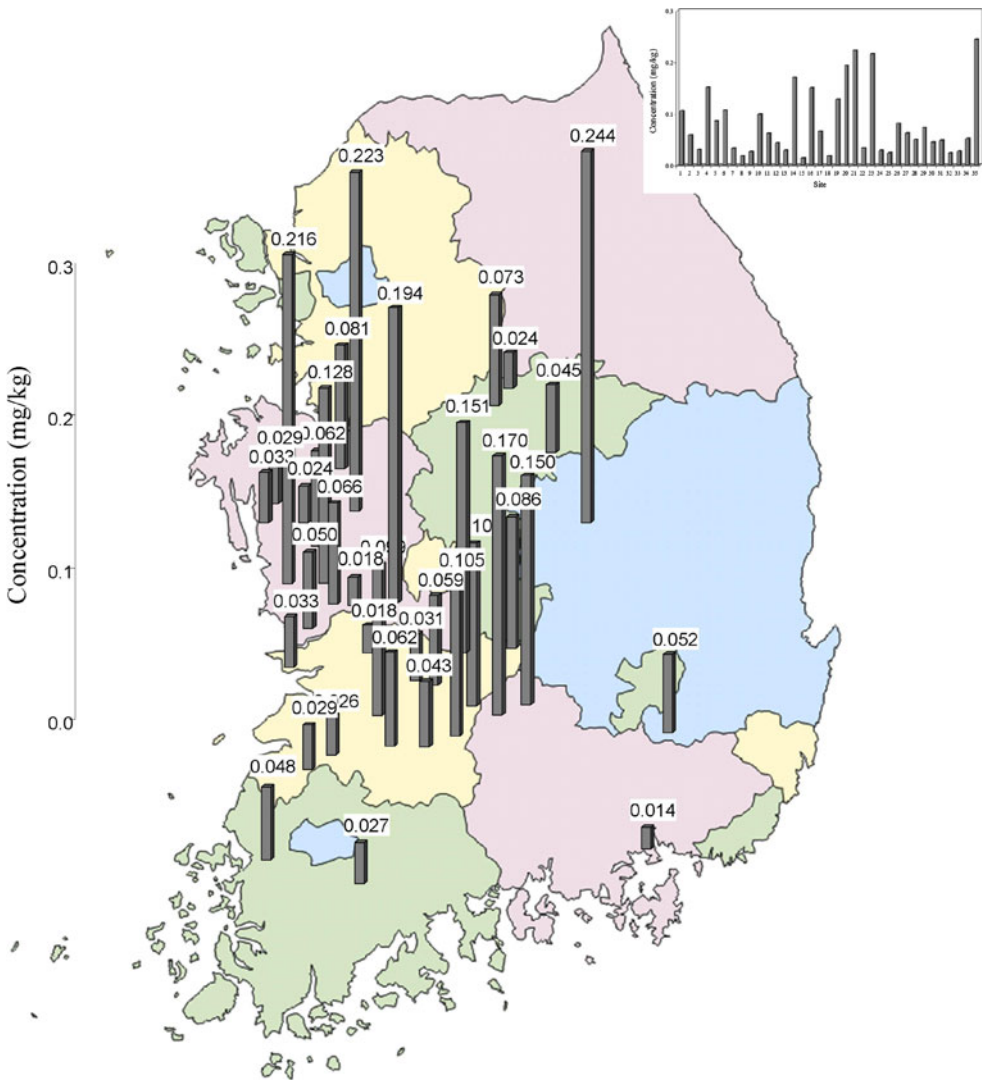

Fig. 1 Spatial distribution of tricyclazole in Korean agricultural field soils. The numbers in parentheses are the arithmetic mean concentration of tricyclazole in the respective sites

0.097, 0.055, 0.024 and 0.147 mg/kg, respectively. Tricyclazole residues concentration was lowest in the Chuncheongbuk-do (0.021 mg/kg) and highest in Gyeongsangbuk-do (0.387 mg/kg). These concentrations are lower compared to those found in other studies (Padovani et al. 2006; Krieger et al. 2000). Irrespective of the soil and field type, tricyclazole concentrations in paddy soil were similar in most of the fields and did not differ significantly during autumn and spring (Fig. 2). Tricyclazole concentrations were much lower in soils than those found in rice grown in the same fields; maximum 0.387 mg/kg compared to 4.245 mg/kg, respectively (Fig. 2) (rice samples were collected from the same sites during September–October and residues were analyzed by National Agricultural Products Quality Management Service (NAQS), Korea). Tricyclazole residues are usually higher in rice compare to those in soil (Phong et al. 2009a).

As the modes of applying insecticides and the formulations used are decisive factors in the persistence of their residues in soils, questionnaire survey were undertaken by interviewing farmers working in these fields in order to understand the formulation, amount, time, and way of spraying tricyclazole. No attempts were made to either regulate or alter the local farming practices. The farmers applied wettable powder (WP) formulation of tricyclazole (500 mg/L) at application rate of 400–800 g per hectare with commercial name 'Beam'. They applied it 3 times throughout the growing seasons (June–July, July–August, August–September; 21 days before harvest).

Tricyclazole residue concentrations in paddy soil were similar in most of the soils from these fields in both autumn and spring seasons, and it fluctuated around average values during these monitoring periods. Linear regression of the data gave almost horizontal lines with low correlation coefficients ($R^2 = 0.3984$, $p < 0.001$). Similar behavior of tricyclazole concentration was also fund by Liu et al. (2008) during the monitoring period of 35 days.

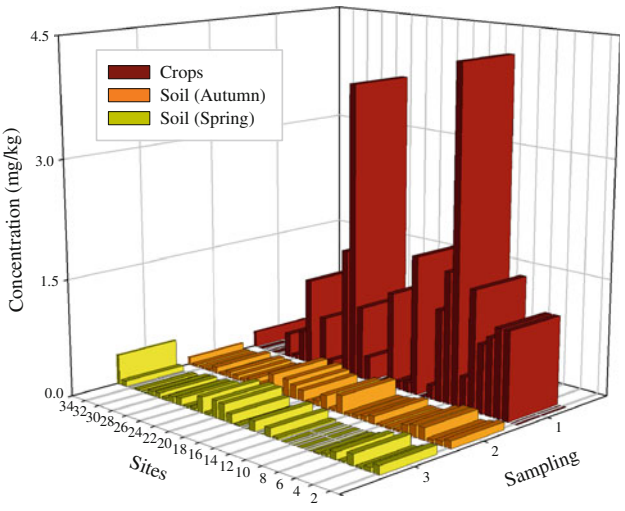

Fig. 2 Persistence of tricyclazole in agricultural field soils (autumn and spring) and crops under different climatic conditions

Variation of tricyclazole concentration in soil with the seasons have been previously demonstrated (Tanabe et al. 2001; Padovani et al. 2006). Tanabe et al. (2001) observed higher concentration in summer compare to autumn, Padovani et al. (2006) found that its concentration was usually high during the application period which decreased significantly few weeks after harvest (November–December). We also observed similar patterns in our study (Fig. 2). Tricyclazole concentration was significantly higher in August–September (in crops) compare to those in October–November (in soils).

Our study aimed to find the influence of cold winter condition on the concentration of tricyclazole over time under field conditions. Interestingly, the concentration did not change significantly after 5 months of cold winter season (November–March) (Fig. 2). The cold climatic conditions seemed to influence on longer persistence of tricyclazole. Effect of cold climatic condition on degradation and persistence of pesticide have been previously evidenced. Studies in the Arctic and Canada have shown that insecticides and herbicides persist 3–8 times longer in cold climates than in temperate ones (Health Canada 1998). Yet another study showed that the cold climatic periods led to higher leaching of pesticides (Stenrod et al. 2008). Further studies in all the four seasons would further put highlight on these scenarios.

In the present study, we found that tricyclazole concentration did not change for as long as 11 months post application in a real field under different climatic condition (June–April), which is longer than those found by Liu et al. (2008), where they found the concentration did not changed for 56 days of monitoring period, and by Padovani et al. (2006), where they observed it persisted in soil for at least 8 months. Clearly, longer monitoring periods are required for determining persistence of tricyclazole in field soil.

The concentration of tricyclazole in soil samples from three fields in Jeollabuk-do and one in Jeollanam-do provinces were below detection level. The soils in these regions are loamy, have high organic matter and low pH, these soil properties could have affected on the decrease of pesticide concentration. Further, tricyclazole gets strongly adsorbed (sorption coefficients K_d 4–96 mL/g) (Phong et al. 2009b; Tomlin 2003) in these type of soil (Roldán et al. 1993), which could have made detection lower (below LOD) (Krieger et al. 2000; Fernandes et al. 2006).

In conclusion, tricyclazole can persist as long as 11 months in field agricultural soils under different climatic conditions (autumn, winter and spring). Our results indicate the influence of cold climatic condition on persistence of tricyclazole. Studies with a longer monitoring period would help us to further understand the fate and persistence of tricyclazole in agricultural field soils under different climatic conditions.

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