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Persistence and Dissipation of O-Sec-Butylphenyl N-Methylcarbamate (BPMC) in Rice Ecosystem

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India is well known as a rice growing area (Prasad 2004). With 45 million hectares of rice area, 90 million tons of production and 2000 Kg/ha of productivity, India is a leading rice growing country in the world (Mishra 2004). After meeting the huge domestic demand, rice exports reached 4.1 million tons during the year 2002 (Mishra 2004). In addition to the contribution of 46% of total food grain production of India, the crop plays a vital role in Indian national food security, as well as livelihood for millions of rural household. Such a noble crop often comes under threat due to the serious pest disease attack. Most of the rice pests are distributed throughout India, however only a few pests are economically important in different regions. The serious pests include gall midge (*Pachydiplosis Oryzae* Wood-Mason), yellow stem borer (*Tryporyza incertulas* Walker), green leaf hopper (*Nephotettix nigropictus* Stal) and brown plant hopper (*Nilaparvata lugens* Stal) in Eastern India (Prasad 2004). To combat with these pests, different carbamate insecticides like carbofuran, carbosulfan, propoxur, BPMC/ fenobucarb etc. have proved their efficiencies (Krishnaiah et al 2003). Among the different carbamate insecticides, BPMC is a unique one for its good knockdown effect but not persistent in nature on rice (Jena et al 1990). BPMC gives good control for stem borer, leaf folder, gundhi bug, hemipteran insects like plant hoppers (Krishnaiah et al 2003).

Literature reports on the behavior of some of the carbamate insecticides (Lee et al 1988; Tayaputch et al 1998; Ito et al 1995; Itagaki et al 1999). Waiting period for carbaryl is reported to be 12 days (Rajukannu et al 1988). DT_{50} values of carbofuran in flooded rice culture were reported as 10 days in paddy water and soil (Johnson et al 1995). Information on the persistence and dissipation pattern of BPMC in rice is scanty. In this present study, the persistence and dissipation pattern of BPMC has been studied in rice ecosystem i.e. in soil, plant/ straw, water, grain, husk and also in the harvested samples to work out the safe waiting period.

MATERIALS AND METHODS

Field studies were conducted during 2003 - 2004 on Kharif Paddy crop (variety - Swarna mashuri) at University Research Farm, BCKV with two treatment doses

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and replicated three times. All the recommended cultural practices for the cultivation of the crop were followed. BPMC 50% EC was sprayed three times (55 DAT, 70 DAT and 85 DAT) each at 0.75 Kg a.i. / ha (T_1) and 1.5 Kg a.i. /ha (T_2) with one untreated control (T_0) was kept following the randomized block design (RBD).

Soil and water samples were taken at 0, 1, 5, 10 and 15 days interval and plant samples were taken at 5, 10, 15 and 30 days after last application. Grain, husk, straw and soil samples at harvest were collected and prepared just after the harvesting of paddy crop. Samples were collected following random sampling technique. Field samples from each of the three replicates per treatment for each substrate at each days interval were colleted and the composite sample were prepared. Here paddy plant sample 500 g, grain 500 g, husk/ straw 500 g, soil 1 Kg and water 2.5 L were taken. No trimming or washing operation was done. For final analysis 50 g valid representative sample were taken by quartering and 500 ml of water for final analysis. Samples for the control were taken in the same days.

50 g air dried soil sample was taken in a conical flask and extracted with 150 ml methanol for 1 hr by using to and fro mechanical shaker. It was then filtered by using Buchner funnel, and residue was washed thoroughly with 2 × 50 ml methanol and filtered again. The combined filtrate was concentrated to 50 ml in a rotary vacuum evaporator at 50°C and then added 50 ml water and partitioned with dichloromethane (100 + 2 × 50 ml). The combined dichloromethane layer was then treated with coagulating solution of 0.112 % ammonium chloride and 0.232 % orthophosphoric acid in a separating funnel and shaken vigorously and then dichloromethane layer was collected in a conical flask after passing through Na_2S0_4. The dichloromethane layer was concentrated and the volume was made up to 5/10/25 ml as required for HPLC analysis with methanol.

Water sample (500 ml) was taken in a separatory funnel and partitioned with 200 ml dichloromethane. The aqueous layer was again extracted with 2 × 150 ml dichloromethane. The combined dichloromethane extract was passed through anhydrous sodium sulfate and then concentrated to about 50 ml volume by rotary vacuum evaporator at 50°C. The dichloromethane extract was then treated with aqueous 0.112 % ammonium chloride and 0.232 % orthophosphoric acid. The mixture was then partitioned with 3 × 100 ml dichloromethane it was concentrated to minimum volume by rotary vacuum evaporator and the volume was made to suitable volume for HPLC analysis.

Grain/husk (50 g) samples were extracted with 150 ml methanol in a soxhlet apparatus for 4 hr The solvent was concentrated to about 25 ml by rotary vacuum evaporator at 50°C. It was then transferred to a separatory funnel and added coagulative solution of 0.112 % ammonium chloride and 0.23% orthophosphoric acid and shaken vigorously for 2-3 min and then added 50 ml water followed by 100 ml dichloromethane and shaken for 2 min and allowed to stand for 10 min. The organic phase was passed through anhydrous sodium sulfate and concentrated to a suitable volume for HPLC analysis.

50 g of plant/ straw sample was blended in warring blender for 2 min with 200 ml methanol. The filtered extract was processed following the same procedure as described for grain/ husk sample.

The residues of BPMC were estimated by HPLC (model- 1050, Hewlett Packard, USA) equipped with an UV/VIS detector at λ_{max} = 254 nm coupled with Chemito - 5000 Data Processor. Shandon Hypersil (250 × 4.6 mm ODS 5µ) reverse phase C_{18} (cartridge) column was used with methanol as the mobile phase at a flow rate of 1 ml min^{-1}. The retention time of BPMC was recorded at 3.255 min.

The average recovery percentage of BPMC was found to be 86.7, 86.5, 88.2, 86.2 and 88.2 for soil, plant/ straw, grain, husk and water samples respectively using standard solution (in methanol) containing 100 µg ml^{-1} of BPMC at the levels of 0.5, 1.0 and 5 µg g^{-1}.

RESULTS AND DISCUSSION

From the dose of 750 g a.i./ ha (T_1) of BPMC, the average residue in paddy soil on the zero day after last application was 1.35 ppm (Table 1), and it declined to 0.011 ppm after 10 days, thus recording about 99.18 percent dissipation losses of initial residues. The BPMC spray 1500 g a.i./ ha (T_2) resulted in 2.326 ppm residues in soil at 0 day of last spray, which dissipated by about 99.44 percent in 10 days. However in both the treatment the residue was not detected in 30 days and also in harvested sample. The rates of dissipation followed a first order kinetics. Statistical analysis of the rate of dissipation (Table 1) showed a linear correlation. Half-life ($T_{1/2}$) values of BPMC in paddy soil were 1.55 and 1.5 days T_1 and T_2 respectively.

Table 1. Dissipation of BPMC 50 EC (BPMC) in paddy cropped soil.

Days after last application	**BPMC spray concentration**			
	T_1= 750 g a.i/ha		**T_2=1500 g a.i/ha**	
	***Mean residue (µg g^{-1}) ± SD**	**% Dissipation**	***Mean residue (µg g^{-1}) ± SD**	**% Dissipation**
0	1.35 ± 0.077		2.326 ± 0.262	
1	0.856 ± 0.046	36.59	1.236 ± 0.114	42.99
3	0.473 ± 0.020	64.96	0.813 ± 0.02	65.04
7	0.14 ± 0.037	89.62	0.363 ± 0.046	84.39
10	0.011 ± 0.0026	99.18	0.013 ± 0.0049	99.44
30	ND	100	ND	100
Harvest	ND	100	ND	100
Y = 3.19 – 0.193 x			Y = 3.4312 – 0.196 x	
$T_{1/2}$ = 1.55 days			$T_{1/2}$ = 1.5 days	

* Data are average of three replication

Table 2. Dissipation of BPMC 50 EC (BPMC) in plant (paddy).

Days after last application	BPMC spray concentration			
	T_1= 750 g a.i/ha		T_2=1500 g a.i/ha	
	*Mean residue ($\mu g\ g^{-1}$) ± SD	% Dissipation	*Mean residue ($\mu g\ g^{-1}$) ± SD	% Dissipation
5	0.71 ± 0.054		1.587 ± 0.147	
10	0.483 ± 0.053	31.9	1.113 ± 0.182	29.9
15	0.26 ± 0.049	63.4	0.627 ± 0.105	60.5
30	0.147 ± 0.029	79.3	0.277 ± 0.021	85.7
Harvest	ND	100	ND	100
$Y = 1.93 - 0.026\ x$			$Y = 2.32 - 0.03\ x$	
$T_{1/2}$ = 11.58 days			$T_{1/2}$ = 10 days	
T_{MRL} = 5.85 days			T_{MRL} = 16.73 days	

* Data are average of three replication

Table 3. Dissipation of BPMC 50 EC (BPMC) in water in paddy crop.

Days after last application	BPMC spray concentration			
	T_1= 750 g a.i/ha		T_2=1500 g a.i/ha	
	*Mean residue ($\mu g\ g^{-1}$) ± SD	% Dissipation	*Mean residue ($\mu g\ g^{-1}$) ± SD	% Dissipation
0	0.0123 ± 0.0061		0.058 ± 0.0081	
1	0.0043 ± 0.002	65.04	0.0076 ± 0.0094	84.8
3	ND	100	ND	100
7	ND	100	ND	100
10	ND	100	ND	100
30	ND	100	ND	100
Harvest	ND	100	ND	100

* Data are average of three replication

From the results shown in Table 2 it was found that the spray application of BPMC 50 EC resulted in deposits of 0.71 and 1.587 ppm for T_1 and T_2 respectively after five days of the last application. After 10 days of application, the residue dissipated by about 31.9 and 29.9 percent for T_1 and T_2 respectively. At 30 days after the last spray, the residue was 0.147 ppm for T_1 thus recording about 79.3 percent dissipation losses of initial residues. T_2 resulted in 85.7 percent dissipation after 30 days of the last spray. However the residue was not detected in harvested sample for any of the treatment doses.

Half-life ($T_{1/2}$) values of BPMC in paddy plant were recorded as 11.58 days and 10 days for T_1 and T_2 respectively. The rates of dissipation followed a first order kinetics. The dissipation pattern almost follows the same as described by Ueji et al 1980, who reported that the disappearance of BPMC in rice plant was rapid and residue level of BPMC was below 0.2 ppm 15 days after treatment (Ueji et al 1980). The MRL value of BPMC in rice is 0.5 ppm (Oh et al 2003). The safe waiting period (T_{MRL}) based on MRL value was about 5.85 days for T_1 and 16.73 days for T_2. The results match with the 14 days recommended pre harvest interval (PHI) values of BPMC in Rice (Ekanayaka et al 2004).

The results of dissipation of BPMC 50 EC (BPMC) in water in Paddy crop have been summarized in Table 3. The initial deposition was found as 0.0123 ppm for T_1 and 0.05 ppm for T_2. After 1 day of the last application the residues dissipated by 65.04% and 84.8% showing a value of 0.0043 ppm and 0.0076 ppm for T_1 and T_2 respectively. The residues declined below the detection limit on 3 days after the last application irrespective of the treatment doses.

From the above study it has been revealed that the residues in either soil or water or in plant declines progressively with time, taking residues at 0 day as initial residues. It has been found that 1.5 - 1.55 days were required for about 50% dissipation of BPMC in soil. About 99% of residues had been dissipated after 10 days in soil in both the doses. No residues were detected after 30 days in soil and 3 days in water. In case of plant, the half-life values were calculated as 11.58 days and 10 days for T_1 and T_2 respectively. The safe waiting period is 5.85 days and 16.73 days for T_1 and T_2 respectively. So it may be concluded that BPMC can be used safely in rice ecosystem without causing any residue problem.

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