Residues of grain protectants on paddy

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Abstract

Storage scale experiments have been conducted in the Philippines to evaluate the effect of grain protectants applied by admixture to paddy for the control of storage insects. Treatment combinations were selected on the basis of preliminary laboratory studies. The aim was to protect paddy during 12-months storage.

Treatments included the combinations: chlorpyrifos-methyl 8.13 mg/kg; deltamethrin 0.41 mg/kg plus piperonyl butoxide 10mg/kg; chlorpyrifos-methyl mg/kg plus methoprene 2.198 mg/kg; pirimiphos methyl 7.99 mg/kg plus permethrin 0.998 mg/kg plus piperonyl butoxide 10 mg/kg; and fenitrothion 10.54 mg/kg plus d-phenothrin 1.054 mg/kg plus piperonyl butoxide 10 mg/kg. Diluted insecticides were applied in the grain stream at a rate of 1 L/t to 185 t of grain which were then bagged for storage. Grain moisture content averaged 14% while initial grain temperature averaged 30°C.

Residues of synthetic pyrethroids were extracted from whole grains using petroleum ether, while acetone–acetic acid was used for the extraction of organophosphates. Quantification was by gas chromatography. An electron capture detector was used for detection of pyrethroid residues and flame photometry for organophosphate residues.

The order of stability of insecticides tested was permethrin > deltamethrin > chlorpyrifos-methyl > methoprene > pirimiphos-methyl > fenitrothion. Residual concentrations in paddy after 12 months of storage were much lower than the maximum residue limits set by the Codex Alimentarius Commission of the Food and Agriculture Organization on cereal grains for safe animal and human consumption.

Introduction

Paddy is an important crop in the Philippines. It is a staple food and major source of carbohydrates for most Filipinos. Although paddy is widely grown in the Philippines, there are times when production cannot meet domestic requirements, and rice must be imported.

Mounting postproduction losses attributed largely to insect induced deterioration under adverse storage conditions in the Philippines negate significant increase in rice production. Studies have shown that in spite of pest control practices employed in storage of paddy, significant losses due to insects still occur. A study conducted by the National Post Harvest Institute for Research and Extension (NAPHIRE) revealed that 7% of the initial weight of paddy was lost after 7 months of storage (Caliboso et al. 1985). This estimate does not include associated quality losses. Thus, a more effective treatment is deemed essential in the Philippine grain storage system.

Several studies indicated the efficacy of synergised synthetic pyrethroids combined with organophosphorous insecticides in controlling storage pests (Bengston et al. 1983; Desmarchelier et al. 1981).

NAPHIRE studies also revealed that either admixture or bag stack spraying of grain protectants plus fumigation was effective and economical to use for long-term storage of paddy (Sayaboc et al. 1988, 1990).

However, excessive use of chemicals for insect control may leave substantial amounts of residues on the grain posing hazards to consumers. It is therefore imperative to monitor levels of pesticide residues to ensure safe use of these materials.

This paper summarises the results of residue analyses determined in paddy samples obtained at various storage intervals, from the time of protectant application until the twelfth month of storage. Effective and safe application of grain protectants could assist in ensuring food security in the country and chance the industry's capability to compete on the international grain market.

Materials and Methods

Grain treatment

Commercial quality paddy was treated directly with insecticides in a grain drying facility of the National Food Authority in Santiago, Isabela, Philippines. The treatments applied and quantities of grain treated are summarised in Table 1. Insecticides were diluted with water and sprayed at a rate of 1 L/t onto the grain stream during turning of grain from one bin to empty bin. The spray nozzle was attached where the grain dropped from the conveyor to the elevator. Each treatment took 12–15 hours. Grain temperature and moisture content were monitored.

Storage and sampling

The grain was bagged into 50 kg polypropylene sacks. It was stored for 12 months in a commercial warehouse built from galvanised iron with concrete floors and walls. Storage commenced 1.5 months after treatment.

An initial composite samples of grain was obtained by taking small sub-samples from the tube connected to the conveyor at 15-minute intervals during treatment before the grain enters the bin. Subsequent samples were withdrawn from 36 marked bags at 6-weekly intervals. Samples were collected from the top, side, inner, and centre of the stack and transported to NAPHIRE laboratory for analysis.

Residue analysis

Samples of grain were subjected to residue analysis using the method developed by Desmarchelier et al. (1977). The

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Table 1. Details of treatment, paddy admixture (January 1990).

Quantity of grain (t)	Initial grain temperature (°C)	Treatment/rate of treatment (mg/kg)	Concentration of insecticide in original formulation
178	26–34	Chlorpyrifos-methyl + deltamethrin	200 EC
172	25–35	Chlorpyrifos-methyl + methoprene	225 EC 500 EC
190	25–36	Fenitrothion +	500 EC
		d-phenothrin and	100 EC
		piperonyl butoxide	930 EC
189	28–32	Pirimiphos-methyl +	250 EC
		permethrin + piperonyl butoxide	930 EC
183		Control	

method involved extraction of pesticides by soaking overnight 40 g of whole grain. Residues of synthetic pyrethroids were extracted using petroleum ether. Acetone–acetic acid was used to extract residues of organophosphorous insecticides. The container was shaken occasionally and before aliquots were taken for quantitation.

Residues were determined by gas–liquid chromatography technique. An electron capture detector was suitable for the detection of pyrethroids while the organophosphates were detected by flame photometry.

Methoprene residues were analysed by high performance liquid chromatography (HPLC). Fifty grams of treated samples were ground into a fine powder and extracted overnight with 100 mL hexane. Five millilitres of crude extract were taken and cleaned-up onto a basic alumina Sep Pak. The methoprene fraction was eluted off the column with 15 mL of 8% v/v tetrahydrofuran in hexane. This fraction was collected, evaporated to dryness and diluted to a volume suitable for HPLC analysis.

Results and Discussion

The residue data indicate loss of insecticides ranging from 11 to 30% during application (Table 2). These losses were generally lower than those measured in a previous trial (Sayaboc et al. 1989). The higher insecticide recovery that was observed in the present study is attributed to some variations in the methods of preparing insecticide solutions. Dilution of insecticides was divided into four parts, at 50 L solution per dilution, unlike the first trial where the total volume of insecticides, a 200 L solution, was prepared at once. This modification was made since heating of insecticide solution augmented by the stirring process, was experienced in the past. The residues measured at various periods of storage showed the dependence of pesticide decay with time (Table 3). At the commencement of storage period, with an average of 45 days after grain treatment, the residues of chlorpyrifos-methyl (with deltamethrin), chlorpyrifos-methyl (with methoprene), pirimiphos-methyl fenitrothion, permethrin, deltamethrin and methoprene were 11%, 9%, 25%, 17%, 4%, 7% and 28% lower than their initial values, respectively. The rate of decay exhibited by the candidate insecticides was observed to be rapid at the first three months of storage, followed by a relatively slow phase of decay. The same observation has been noted previously (Ong Seng Hock et al. 1986; Gragasin et al. 1991).

At the end-of-storage period, the detected amount of residues of chlorpyrifos-methyl (with deltamethrin), chlorpyrifos-methyl (with methoprene), pirimiphos-methyl, fenitrothion, permethrin, deltamethrin and methoprene were 14%, 26%, 13%, 3%, 58%, 34%, and 14%, respectively, of their initial values (Table 4). Longer persistence of pyrethroids than organophosphates was very evident. High rate of volatilisation and susceptibility to photolytic decomposition are the two most important characteristics of organophosphates which contribute to their more rapid degradation.

Among the organophosphates tested, chlorpyrifos-methyl was found to be the most stable, followed by pirimiphos-methyl. Fenitrothion was very unstable.

Of the two pyrethroids evaluated, permethrin was much more stable than deltamethrin. Noble et al. (1982) noted that the more rapid decay of deltamethrin residues. Residues of permethrin and deltamethrin detected from final samples in this study were similar to those recovered by Noble et al. at almost the same length of storage time and condition.

Throughout the trial, the levels of insecticide residues detected on treated samples were below the maximum residue limits set by the Codex Alimentarius

Commission of the Food and Agriculture Organisation as safe for human and animal consumption (Table 5).

Summary and Conclusion

Initial residues of insecticides evaluated were lower than the target dosages. The decline of residues from initial samples was not due to rapid decay of insecticides since the interval

Table 2. Calculated application rates vs. residues measured analytically, sampled immediately after treatment.

Treatment	Calculated application rate (mg/kg)	Residue measured immediately after treatment (mg/kg)	Per cent recovered at time zero
A. Chlorpyrifos-methyl (w/deltamethrin)	8.13	6.60	81
B. Cholrpyrifos-methyl (w/methoprene)	10.0	7.28	73
C. Pirimiphos-methyl	7.99	5.63	70
D. Fenitrothion	10.54	7.44	71
E. Deltamethrin	0.41	0.29	71
F. Permethrin	0.998	0.73	73
G. Methoprene	2.198	1.96	89

Table 3. Pesticide residues (mg/kg) on paddy at various storage periods.

Insecticide	Days in storage									
	0	5	45	97	144	212	257	288	334	384
A. Chlorpyrifos-methyl(with deltamethrin)	6.60	5.89	4.62	2.93	3.69	2.75	1.26	1.09	0.94	0.94
B. Chlorpyrifos-methyl(with methoprene)	7.28	6.61	4.13	2.30		2.88	3.43	2.86	2.00	1.86
C. Pirimiphos-methyl	5.63	4.25	3.97	2.66	2.83	1.42	0.85	0.87	0.76	0.71
D. Fenitrothion	7.44	6.17	5.17	4.67	1.96	0.79	0.74	0.25	0.22	0.22
E. Permethrin	0.73	0.70	0.60	0.53	0.42	0.39	0.39	0.45	0.39	0.42
F. Deltamethrin	0.29	0.24	0.17	0.17	0.12	0.10	0.1	0.10	0.10	0.10
G. Methoprene	1.96	1.41	1.05	0.86	0.66	0.59	0.49	0.41	0.38	0.35

Table 4. Residues left at the end of storage period(%).

Insecticide	Residues (mg/kg)		Residue at the end of the storage period (%)
	Initial	Final	
A. Chlorpyrifos-methyl (with deltamethrin)	6.60	0.94	14
B. Chlorpyrifos-methyl (with methoprene)	7.28	1.86	26
C. Pirimiphos-methyl	5.63	0.71	13
D. Fenitrothion	7.44	0.22	3
E. Deltamethrin	0.29	0.10	34
F. Permethrin	0.73	0.42	58
G. Methoprene	1.96	0.35	18

Table 5. Residues (mg/kg) left at the end of storage vs. maximum residue limit (mg/kg) set by Codex Alimentarius Commission for cereal grains.

Insecticides	Residues at the end of storage	Maximum residue limit (mg/kg)
A. Chlorpyrifos-methyl(with Deltamethrin)	0.94	10
B. Chlorpyrifos-methyl (with Methoprene)	1.86	10
B. Pirimiphos-methyl	0.71	10
C. Fenitrothion	0.22	10
D. Deltamethrin	0.10	2
E. Permethrin	0.42	2
F. Methoprene	0.35	10

between treatment and sampling was only 15 minutes. It was attributed to loss during spraying where some of the aerosols drifted away from the grains being treated.

Partial degradation is also possible during transport of samples from the treatment site to the laboratory.

Generally, the residues of the candidate grain protectants decreased with time after application. Organophosphates were observed to decay more rapidly than pyrethroids.

Residual concentrations in paddy after 12 months of storage were considerably lower than the maximum residue limits approved by Codex Alimentarius Commission of the Food and Agriculture Organisation. It can thus be concluded that paddy admixed with the candidate insecticides at levels evaluated in the trial was safe for human and animal consumption.

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