Degradation of Organophosphate Pesticides in Cereal Grains during Milling and Cooking in India[1]

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Summary

Samples of paddy (rough rice), wheat, and sorghum were treated with different concentrations of malathion, Gardona, and Sumithion for protection against insect infestation during storage. Subsequently, samples were milled, cooked, and analyzed by gas-liquid chromatography to determine residues remaining in the final products. Malathion and Gardona treatments ranged from 10 to 80 p.p.m.; Sumithion treatments, from 2 to 16 p.p.m. During machine milling, residues in wheat and sorghum were decreased from 30 to 70%. Because residues were concentrated in the hull and bran of the paddy, relatively little remained on polished rice after milling. Even with treatments of 80 p.p.m. residues on polished rice were never more than 4 p.p.m. Milled products from each grain were cooked using traditional Indian methods. Preparations involving boiling or steaming (wet cooking) resulted in complete degradation (loss) of residues of all three protectants so far as detectable with methods sensitive to less than 0.1 p.p.m. Dry cooking methods, used in preparing chapatties from wheat and sorghum, resulted in average losses of 43 to 75% of residues.

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The Indian Government's Prevention of Food Adulteration rules (P.F.A.) now forbid admixture of any insecticide with food materials. Consequently, grain cannot legally be treated with pesticides for protection during storage, although use of fumigants is permitted (1). That contrasts with regulations in many other countries, including the U.S., where treatment with malathion up to 8 p.p.m. on stored grain is allowed (2). Part of the rationale behind the P.F.A. regulations against the use of pesticides on stored products was that sufficient data from pesticides use in India were not available. Meanwhile, various insecticides have been misused in India as grain protectants. In 1967 a government commission recommended that, to combat indiscriminate use of persistent organochlorine pesticides on stored grain, the use of malathion and pyrethrums should be encouraged after suitable studies had been carried out (3). Several studies conducted in India indicate that malathion can protect stored grain while residues are kept acceptably safe for human consumption as determined by the Codex Alimentarius Commission (4–6). The study (in India) reported here was to determine how much of the residue from storage treatments with malathion, Gardona, or Sumithion is degraded while the grain is being prepared for human consumption by milling and cooking.

Materials and Methods

Grain. The variety of paddy (rough rice) used was Bangaru Sanna, grown locally in Mysore State, South India. The D 340 sorghum also was obtained locally. The wheat was a hard amber variety from Maharashtra. Care was taken to avoid grain that had been treated with pesticide. Both bioassay and residue tests were performed on samples to be certain of no effects from previous, undisclosed treatments.

Treatment with Protectants. Five-kilogram samples of each grain were treated with three different amounts of each of the three protectants: 10, 40, and 80 p.p.m. for malathion[4] and Gardona;[5] 2, 8, and 16 p.p.m. for Sumithion.[6] Protectants were freshly prepared emulsions of primary (analytical) grade pesticide applied to the grain as it was tumbled in a mixer.

Bioassay. Cultures of red flour beetles (*Tribolium castaneum* Hbst.) and rice weevils (*Sitophilus oryzae* L.) were used for bioassay tests. Each batch of treated grain was sampled after 24 hr., 1 month, and 2 months. In each instance 10 adults of each species were exposed to the treated grain after samples had been partially ground and placed into a vial. Each test was replicated three times. After 7 days, dead insects were counted.

Milling. Sorghum and wheat were milled using an electrically powered disc mill, a type common in cities and villages throughout India. The grain sample (500 g.) was ground until 90% passed through a 32-mesh sieve. Paddy was milled by hulling 1-kg. samples in a McGill Sheller and polishing 700 g. of the resulting brown rice in a McGill No. 3 polisher set to give a 4% polish.

Cooking. Chapatties were prepared from 30 g. of flour. Distilled water was added to give a suitable dough, which was formed into a thin chapatti and cooked on a griddle without oil. Besides chapatties, sorghum dough was formed into balls and cooked by boiling. Rice was prepared both by boiling and as a gound paste, which was fermented, formed into balls, and steamed (a South Indian preparation called *iddli*). All cooking trials were conducted in triplicate and results were averaged.

Extraction and Cleanup. Methanol is an efficient solvent to extract malathion from grain (7). Residues were extracted for gas-liquid chromatographic analyses by agitating 5 g. of each sample with 10 ml. of methanol for 2 hr. The residue, after being filtered, was washed twice with 5-ml. aliquots of methanol and the washings were combined with the original filtrate. Cooked samples were dried and ground to pass through a 32-mesh sieve before extraction. Cleanup of the methanol extracts was accomplished by agitating the filtrate with 1 g. of Nuchar attaclay for 2 hr. After filtering, the volume was adjusted to 25 ml. with methanol and internal standard was added. The samples were then analyzed by gas-liquid chromatography.

Analysis. A Varian Aerograph Model 1400 gas-liquid chromatograph equipped with an alkali flame ionization detector with cesium bromide salt tip was used for analyses. The Pyrex glass column (6 ft. × 0.25 in. o.d., 2 mm. i.d.) was packed with 1.5% OV-225 on high-performance Chrom W. The column oven was operated at 210°C., the injection port at 230°C., and the detector at 240°C. Hydrogen flow was adjusted to 36 ml. per min. at the detector. Flow rates of air and nitrogen were adjusted over ranges of 200 to 300 ml. per min. and 14 to 40 ml. per min., respectively, as required to adjust the detector for satisfactory response. A 5-μl. Hamilton syringe was used to inject 2-μl. samples of the methanol extract into the chromatograph. Amounts of residue in each sample were determined by comparing the area of the peak produced by the residue to the area of the peak resulting from the internal standard. That ratio indicated the concentration of residue when compared with a calibration curve prepared from different concentrations.

[4] S-(1,2-Dicarbethoxyethyl) O,O-dimethyldithiophosphate; phosphothion; donated by Agricultural Division, American Cyanamid Co., Princeton, N. J.

[5] O,O-Dimethyl 2-chloro-1-(2,4,5-trichlorophenyl) vinyl phosphate; Shell SD 8447; donated by Woodstock Agricultural Research Centre (Shell), Sittingbourne, Kent, England.

[6] Fenitrothion; O,O-dimethyl O-(4-nitro-m-tolyl) phosphorothioate; Bayer 41831; donated by Sumitomo Chemical Co., Osaka, Japan.

TABLE I. RESULTS OF PERIODIC BIOASSAY TESTS FOR RESIDUES OF INDICATED INSECTICIDES USED TO CONTROL RED FLOUR BEETLES AND RICE WEEVILS IN PADDY (ROUGH RICE)

Insecticide	Treatment Amount p.p.m.	Test Insect	% Mortality at[1] 0 Month	1 Month	2 Months
Malathion	10	RFB[2]	97	90	10
		RW[3]	100	100	97
	40	RFB	100	100	97
		RW	100	100	100
	80	RFB	100	100	100
		RW	100	100	100
Gardona	10	RFB	100	97	73
		RW	100	100	97
	40	RFB	100	100	100
		RW	100	100	100
	80	RFB	100	100	100
		RW	100	100	100
Sumithion	2	RFB	27	10	3
		RW	97	53	13
	8	RFB	100	100	23
		RW	100	100	90
	16	RFB	100	100	100
		RW	100	100	100

[1] 0% mortality in control vials
[2] Red flour beetles (*Tribolium castaneum*)
[3] Rice weevils (*Sitophilus oryzae*)

TABLE II. RESULTS OF PERIODIC BIOASSAY TESTS FOR RESIDUES OF INDICATED INSECTICIDES USED TO CONTROL RED FLOUR BEETLES AND RICE WEEVILS IN WHEAT

Insecticide	Treatment Amount p.p.m.	Test Insect	% Mortality at[1] 0 Month	1 Month	2 Months
Malathion	10	RFB[2]	100	97	70
		RW[3]	100	100	100
	40	RFB	100	100	100
		RW	100	100	100
	80	RFB	100	100	100
		RW	100	100	100
Gardona	10	RFB	100	100	90
		RW	100	100	100
	40	RFB	100	100	100
		RW	100	100	100
	80	RFB	100	100	100
		RW	100	100	100
Sumithion	2	RFB	60	7	3
		RW	100	40	7
	8	RFB	100	100	100
		RW	100	100	100
	16	RFB	100	100	100
		RW	100	100	100

[1] 0% mortality in control vials.
[2] Red flour beetles (*Tribolium castaneum*).
[3] Rice weevils (*Sitophilus oryzae*).

of the pesticide being assayed plus a constant amount of internal standard. Malathion was used as an internal standard for samples containing Gardona. Gardona was used as an internal standard for samples containing malathion or Sumithion.

Results and Discussion

Bioassay Tests. Tables I and II give mortality at 0, 1, and 2 months for rice weevils and red flour beetles exposed to paddy and wheat treated with each of the three levels of the three pesticides. Table III gives similar information for sorghum at 0 and 1 month. Highest concentrations of the three pesticides killed 100% of the insects. Intermediate concentrations of all three pesticides were completely effective in sorghum and wheat, but Sumithion at 8 p.p.m. in paddy had begun to lose effectiveness after 2 months, particularly to red flour beetles. At the lowest concentration, Sumithion was relatively ineffective in controlling paddy infestation. By the end of the test periods Sumithion at 2 p.p.m. lost effectiveness with the other grains, too. At lowest concentration, malathion and Gardona also began to lose effectiveness at the end of the test. In general, treatments of paddy were less effective than equivalent treatments of the other two grains. This probably was due in part to the method of application and mixing. Because rice hull is rougher than sorghum or wheat, more chemical presumably wore off (dusted off) as paddy was tumbled.

Loss of Residues during Milling. Tables IV and V show residues detected in whole and milled grains (wheat and sorghum). The average residue losses during grinding were:

Wheat treated with	Malathion	71%
	Gardona	30%
	Sumithion	62%
Sorghum treated with	Malathion	40%
	Gardona	39%
	Sumithion	28%

Minor adjustments in the clearance of the grinding discs made a noticeable difference in heating of the grain during grinding. Variation in residue loss (breakdown) may have partially resulted from that. Milling (wheat) with a hand-operated grinding stone (chakki) resulted in a much lower loss of malathion and Sumithion.

Table VI shows the amounts of malathion, Gardona, and Sumithion applied to paddy and residues remaining in the polished rice, from the protectant migrating through the hull and bran into the endosperm. However, even 80 p.p.m. of malathion left less than 4 p.p.m. residue in the polished rice — less than 50% of the 8 p.p.m. authorized by many countries (2).

Degradation of Residues during Cooking

Chapatti-Making. Table VII shows losses of pesticide residues during preparation of chapatties from wheat flour. Average losses varied from 51 to 75% (Table VII), and 43 to 74% for sorghum flour (data not shown). However, breakdown of residues varied widely during preparation of chapatties, as shown by large standard deviations. Preparation of chapatties varies considerably from household to household and from one part of India to another, so the variation we noted may be typical.

Boiling and Steaming. Within detectable units (less than 0.1 p.p.m.) of the methods we used, residues of all three protectants were completely broken down during the wet-cooking methods. Peaks due to protectants were not present in gas-liquid chromatograms of samples extracted from boiled rice, iddli (steamed, fermented rice), and boiled sorghum balls.

Conclusions

The bioassay tests indicated that 10 p.p.m. of malathion or Gardona, or 8 p.p.m. of Sumithion, when applied and for a period of approximately 2 months afterwards, killed the stored products insects tested. Sumithion at 2 p.p.m. killed rice weevils in wheat and sorghum at the time of application, but its effectiveness began to decrease in less than 2 months. When applied at 2 p.p.m. it did not eliminate all red flour beetles even at the time of application. For longer periods of protection, more Sumithion probably should be applied.

Residue losses during power grinding ranged from 30 to 70%. That, combined with losses of 40 to 75% during the

TABLE III. RESULTS OF PERIODIC BIOASSAY TESTS FOR RESIDUES OF INDICATED INSECTICIDES USED TO CONTROL RED FLOUR BEETLES AND RICE WEEVILS IN SORGHUM

Insecticide	Treatment Amount p.p.m.	Test Insect	% Mortality at[1] 0 Month	1 Month
Malathion	10	RFB[2]	100	93
		RW[3]	100	100
	40	RFB	100	100
		RW	100	100
	80	RFB	100	100
		RW	100	100
Gardona	10	RFB	100	97
		RW	100	100
	40	RFB	100	100
		RW	100	100
	80	RFB	100	100
		RW	100	100
Sumithion	2	RFB	97	13
		RW	100	60
	8	RFB	100	100
		RW	100	100
	16	RFB	100	100
		RW	100	100

[1]0% mortality in control vials
[2]Red flour beetles (*Tribolium castaneum*)
[3]Rice weevils (*Sitophilus oryzae*)

TABLE VI. RESIDUES OF MALATHION, GARDONA, AND SUMITHION DETECTED IN POLISHED RICE 0, 1, AND 2 MONTHS AFTER APPLICATION TO PADDY

Insecticide	Treatment Amount p.p.m.	Residue In Paddy at 0 Months p.p.m.	Residue Detected in Polished Rice at: 0 Month p.p.m.	1 Month p.p.m.	2 Months p.p.m.
Malathion	10	3.5	b.d.[a]	0.16	1.55
	40	9.5	0.19	n.d.[b]	3.0
	80	37.5	0.36	0.75	3.24
Gardona	10	6	b.d.	b.d.	b.d.
	40	26.5	0.8	1	b.d.
	80	52.5	2.3	1.6	1.65
Sumithion	2	1.2	b.d.	b.d.	b.d.
	8	3.4	0.22	b.d.	0.21
	16	9.6	0.48	0.4	0.26

[a]b.d. = below detectability.
[b]n.d. = not determined.

TABLE IV. LOSSES OF INDICATED INSECTICIDE RESIDUES DURING MACHINE GRINDING OF WHEAT

Insecticide	Treatment Amount p.p.m.	Insecticide Residue Recovered from: Whole grain p.p.m.	Machine-ground grain p.p.m.	Loss of Residue: p.p.m.	%	Avg. %	Std. Dev. %
Malathion	10	5.8	2.2	3.6	62		
	40	31.9	9.3	22.6	71	71	8.5
	80	77.1	16.5	60.6	79		
Gardona	10	18	13.5	5.5	31		
	40	39	27.5	11.5	29	30	1.2
	80	65	45	20	31		
Sumithion	2	2	1	1	50		
	8	8.3	3	5.25	64	62	11.6
	16	15.5	4.2	11.3	73		

TABLE V. LOSSES OF INDICATED INSECTICIDE RESIDUES DURING MACHINE GRINDING OF SORGHUM

Insecticide	Treatment Amount p.p.m.	Insecticide Residue Recovered from: Whole Grain p.p.m.	Machine-ground grain p.p.m.	Loss of Residue: p.p.m.	%	Avg. %	Std. Dev. %
Malathion	10	5.76	3.4	2.23	41		
	40	22.4	13.5	8.9	40	40	1.5
	80	53.3	33	20.3	38		
Gardona	10	6.5	2.75	3.75	58		
	40	32.5	25.5	7	22	39	17.5
	80	85	53	32	38		
Sumithion	2	2.5	1.8	0.7	28		
	8	9.25	6.5	2.75	30	28	2.0
	16	15.5	11.5	4	26		

TABLE VII. LOSS OF INDICATED INSECTICIDE RESIDUES DURING THE PREPARATION OF CHAPATTIES FROM *WHEAT FLOUR*

Insecticide	Treatment Amount p.p.m.	Months after Treatment	Insecticide Residue Recovered from: Machine-ground grain p.p.m.	Chapatti p.p.m.	Loss during Cooking: p.p.m.	%	Avg. %	Std. Dev. %
Malathion	10	0	2.2	1.5	0.7	32		
		1	0.8	0.23	0.57	71		
		2	0.53	0.23	0.3	57		
	40	0	9.3	5.8	3.5	38		
		1	3.5	1.3	2.2	63	51	24.0
		2	1.85	0.95	0.9	49		
	80	0	16.5	16	0.5	3		
		1	12	3.5	8.5	71		
		2	7.5	1.6	5.9	79		
Gardona	10	0	13.5	b.d[a]	13.5	100		
		1	5	2.85	2.15	43		
		2	2.35	0.65	1.70	72		
	40	0	27.5	1.7	25.8	94		
		1	27.5	7.5	20	73	75	18.3
		2	8	3	5	63		
	80	0	45	3	42	93		
		1	50	12.5	37.5	75		
		2	18	6.5	11.5	64		
Sumithion	2	0	1	0.53	0.47	47		
		1	0.2	b.d.	0.2	100		
		2	0.13	0.13	0	0		
	8	0	3	1.5	1.5	50		
		1	1.1	0.09	1.01	92	52	35.1
		2	0.58	0.38	0.2	34		
	16	0	4.2	3.6	0.6	14		
		1	1.9	0.23	1.67	88		
		2	1.08	0.65	0.43	40		

[a]b.d. = below detectability.

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preparation of chapatties from wheat and sorghum flour, made total residue losses range from 59 to 93% for whole grain (wheat and sorghum) processed to chapatties. With rice products, wet cooked, all three protectants were totally degraded, except that metabolites, undetected with the equipment we used, may have formed. In India, steam cooking of rice has been reported to almost completely (>95%) destroy malathion (8). Large (75 to 78%) losses of malathion were observed during preparation of chapatties from wheat or wheat flour (5, 9).

Recommendations now being advanced to amend the P.F.A. rules to allow at least 8 p.p.m. of malathion as a grain protectant in India seem to be justified — particularly when one considers the hazards presently posed by misuse of such other pesticides as DDT, BHC, endrin, lindane, and others to control insect infestation in stored grain. Pesticides often are misused because of lack of proper guidance in their use by the farmer.

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