ORGANOPHOSPHATE INSECTICIDE RESIDUES IN GRAINS. II. EFFECT OF COOKING ON MALATHION AND PIRIMIPHOSMETHYL RESIDUES IN RICE[1]

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Washing the rice prior to cooking reduces residue levels considerably and cooking could also cause degradation of pesticide residues. Malathion residues was reduced by 84.4 percent with washing and cooking compared to 61 percent only for cooking while pirimiphos-methyl was reduced by 52.3 percent and 12.5 percent, respectively.

Stored harvested rice is subject to depredations by several stored product pests. Since rice provides a larger proportion of human food than any other single crop and is the staple food of over half of the world's population, its protection from these storage pests is of considerable importance. In the Philippines, the importance of stored rice protection is evident from the fact that as of June, 1978, the national cereal buffer stocks maintained by the National Grains Authority in warehouses are 12.8 million 50-kg cavans of unmilled rice worth ₱70.6 million and 2.36 million 50-kg cavans of milled rice worth ₱248.5 million.

To protect the stocks especially of milled rice from such insect pests as the rice weevil, *Sitophilus zeamais*, and the red flour beetle, *Tribolium castaneum*, insecticides are sometimes applied as admixtures or sack treatment. Insecticide application may also be done on the warehouse premises and contamination of the stocks is a possibility. A continuous pesticide residue monitoring program is therefore advisable.

A previous report has shown that the mixture of pirimiphos-methyl with corn at 10, 15 and 30 ppm gave residues in the range of 0.6 to 2.6 mg/kg and 0.4 to 2.5 mg/kg after three and six months storage (Varca et al., 1975). The same study found that corn stored for three, six, and nine months in sacks dipped in two and four percent malathion solutions had residues from 1.0 to 1.4 mg/kg. These residue levels are lower than the internationally proposed maximum residue limits. Also, as far as residues are concerned, cooking could be an added safety measure. This is evaluated in this study.

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MATERIALS AND METHODS

Insecticide treatment and cooking. One kg of milled, polished rice was sprayed with malathion and pirimiphos-methyl solutions to obtain insecticide concentrations of 10, 20 and 30 ppm in grains. The samples were air-dried and stored at room temperature for one week. One hundred g representative samples were taken for cooking. For each fortification level, two processing procedures were evaluated 1) washing before cooking and 2) cooking without washing. In the former, the rice was washed twice with 200 ml of tap water. The treated rice was simmered with 200 ml of tap water using an automatic rice cooker for about 15 minutes. The amount of water used was 1.5 times the volume of uncooked rice. Washing was omitted for (2) above. Triplicate determinations were carried out on each sample.

Extraction. a. Rice — Fifty g of cooked rice was taken for analysis. Fifty g representative samples of treated rice were also analyzed to determine the amount of residues before cooking. The procedure followed was that reported by Varca et al., (1975). Samples were shaken with 100 ml of methanol in a mechanical shaker for one h, allowed to stand for two h, the solvent was decanted off, and the solids were washed twice with 25 ml of methanol. The organic phases were combined, the volume was noted, and aliquots of the extract were injected into the gas chromatograph without cleanup.

b. Wash-Water — The method of analysis was taken from the "Manual of Analytical Methods for the Analysis of Pesticide Residues in Human and Environmental Samples" (Environmental Protection Agency, 1974). One hundred ml aliquots were shaken twice for two min with 100 ml of 15 percent methylene chloride-hexane solvent mixture in a separatory funnel, and the layers were allowed to separate. The aqueous layer was drawn off into a second separatory funnel, and extracted with 50 ml of hexane. The methylene chloride-hexane extracts were combined, filtered through anhydrous sodium sulfate powder, concentrated to dryness, and dissolved in five ml of methanol. Aliquots of the extracts were injected into the gas chromatograph.

Gas chromatography. A Varian 1400 gas chromatograph equipped with an alkali flame ionization detector was used with the following gas chromatographic parameters.

Column	:	3' x 1/8" O.D. Stainless steel packed with 3% OV-1 on 80/100 Gas Chrom Q	
Temperatures (°C)	:	Injector	250
		Column	220
		Detector	240

Flow rates (ml/min)	:	Nitrogen	37
		Hydrogen	66
		Compressed Air	to 250
Retention time (min)	:	Malathion	2.7
		Pirimiphos-methyl	2.1
Minimum Detection Limits (5: 1 signal-noise ratio)		*Malathion*	
		Water —	0.3 mg/kg
		Rice —	0.5 mg/kg
		Pirimiphos-methyl	
		Water —	.03 mg/kg
		Rice —	.08 mg/kg

Quantitation was done by the use of a previously constructed calibration curve confirmed by injecting standards after two sample injections to correct for changes in detector sensitivity. Representative chromatograms are shown in Figures 1 and 2.

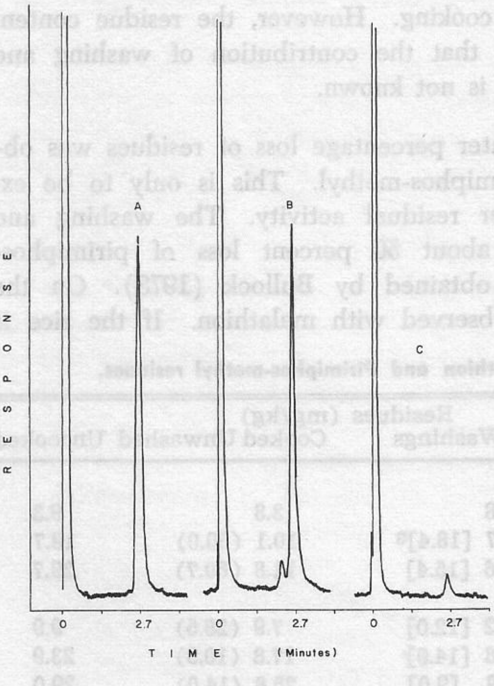

Fig. 1. Typical gas chromatograms of A) Standard B) Polished rice C) Cooked rice with Malathion.

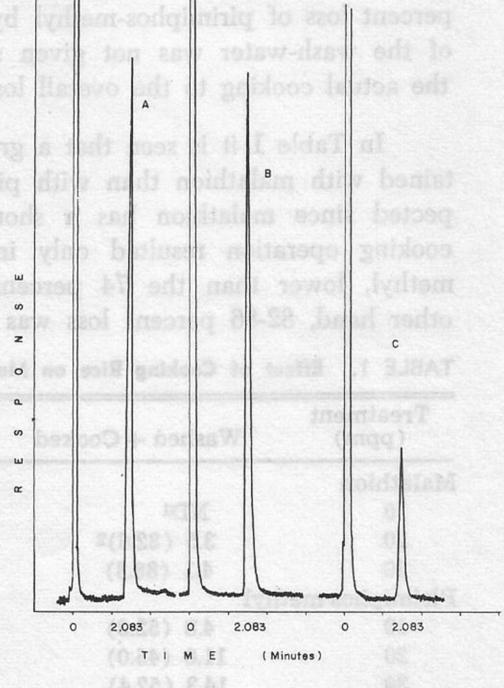

Fig. 2. Typical gas chromatograms of A) Standard B) Polished rice C) Cooked rice with Pirimiphos methyl

RESULTS AND DISCUSSIONS

Malathion is one of the more widely used insecticide against a variety of pests including stored products insects. While it is still generally useful as a stored products protectant, enjoying as it does the advantage of low mammalian toxicity, there are already reports of resistance development (Pieterse et al., 1972; Waterhouse, 1973). Its solubility in water is 145 mg/L (Gunther et al., 1968) and vapor pressure is 4×10^{-5} Torr at 30°C (Martin and Worthing, 1977).

Pirimiphos-methyl is a fast-acting broad-spectrum organophosphate insecticide with both contact and fumigant action. While it possesses limited biological persistence in leaf surfaces, it has a long residual activity when applied to stored grains. As a result, the most important potential use is as stored grain protectant. It is generally regarded as a better compound than malathion because 1) it has longer residual activity, 2) lower application rates are required and 3) effective against malathion resistant strains of some stored products pests (FAO/WHO 1976). Pirimiphos-methyl decomposes above 100°C, has a vapor pressure of approximately 1×10^{-4} Torr at 30°C, and is miscible in water at approximately 5 mg/L at 30°C.

In a cooking study with polished rice, Bullock (1973) showed a 74 percent loss of pirimiphos-methyl by cooking. However, the residue content of the wash-water was not given so that the contribution of washing and the actual cooking to the overall loss is not known.

In Table 1 it is seen that a greater percentage loss of residues was obtained with malathion than with pirimiphos-methyl. This is only to be expected since malathion has a shorter residual activity. The washing and cooking operation resulted only in about 50 percent loss of pirimiphos-methyl, lower than the 74 percent obtained by Bullock (1973). On the other hand, 82-86 percent loss was observed with malathion. If the rice is

TABLE 1. **Effect of Cooking Rice on Malathion and Pirimiphos-methyl residues.**

Treatment (ppm)	Residues (mg/kg) Washed + Cooked	Washings	Cooked Unwashed	Uncooked
Malathion				
10	ND[1]	3.8	3.8	9.3
20	3.5 (82.6)[2]	3.7 [18.4][3]	10.1 (50.0)	19.7
30	4.1 (86.3)	4.6 [15.4]	11.8 (60.7)	29.7
Pirimiphos-methyl				
10	4.8 (52.3)	1.2 [12.0]	7.9 (28.5)	9.9
20	11.0 (45.0)	2.8 [14.0]	17.8 (10.9)	23.9
30	14.3 (52.4)	2.9 [9.0]	25.8 (14.0)	29.0

[1] ND = $<$ 0.5 mg/kg
[2] Figures in parenthesis refer to percent loss relative to fortification level.
[3] Figures in brackets refer to percent recovered relative to fortification level.

cooked without washing, loss of malathion residues was 50-60 percent but only 10 to 28 percent for pirimiphos-methyl, further indicating the greater stability of pirimiphos-methyl.

The data in Table 1 also shows a material balance. The percent loss through the washing of the rice were 15 to 18 percent and 9 to 14 percent for malathion and pirimiphos-methyl, respectively. This difference in removal of residues could be attributed to the higher water solubility of malathion. On the other hand, for malathion the residues remaining in the cooked rice was only approximately 15 percent of the original fortification level. The difference of about 64 to 71 percent could be attributed either to degradation as a result of cooking or volatilization. This corresponds to 31 to 43 percent for pirimiphos-methyl.

CONCLUSIONS

It is evident from this study that the simple practice of washing rice before cooking results in a sizable reduction in residue levels at least for malathion and pirimiphos-methyl. Malathion is more readily degraded than pirimiphos-methyl. Slightly higher losses through washing was obtained with malathion. The heating effect of cooking is mainly responsible for the loss of the two organophosphate insecticides.

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