Bull. Environ. Contam. Toxicol. (1988) 41:299–303

Environmental Contamination and Toxicology

Persistence of Pirimiphos-methyl in Stored Potatoes

Demetrios G. Hadjidemetriou

Central Chemistry Laboratory, Agricultural Research Institute, Nicosia, Cyprus

The potato tuber moth Phthorimaea operculella (Zeller) was introduced to Cyprus most probably in 1916 (Morris 1933). The pest was quickly established and has become dominant in the potato area. The chemicals used in Cyprus in the early fifties for stored potatoes were DDT and parathion; these were later substituted by low mammalian toxicity pesticides such as carbaryl, tetrachlorvinhpos and malathion. Laboratory tests performed with monocrotophos, diazinon and pirimiphos-methyl showed that the potato tuber moth was susceptible to these insecticides (Ali 1974/1976). Pirimiphos-methyl is an insecticide of low toxicity and is used widely for the protection of stored products and in public health (Anonymous 1977). The degradation of pirimiphos-methyl was studied in stored grains (Leahy and Curl 1982; Sowumi and Fetuga 1983) and was found to be very slow.

Farmers in Cyprus keep part of their potato production for local consumption in clumps out in the field, in sheds, and cold rooms. The major part is exported. The purpose of this research is to study, under local conditions, the persistence of ^{14}C-pirimiphos-methyl in stored potatoes.

MATERIALS AND METHODS

Analytical grade reagents were used, and organic solvents were redistilled in glass prior to use. ^{14}C-pirimiphos-methyl radiolabelled in the 2 position of the pyrimidine ring, was used in this study. It was supplied by ICI Ltd., and purified by normal phase thin-layer chromatography using hexane + diethyl ether + methanol (10+1+1). Florisil was heated at 140°C overnight and stored at 102°C. A batch was deactivated, by adding water (1.5%) and mixing on a shaker for one hour on the day it was required. The scintillation solution consisted of PPO (5.5g) and POPOP (0.5g) in scintillation grade toluene (1000 ml). Fluka TLC aluminium plates pre-coated with silica gel (0.2 mm) and fluorescent indicator (254 nm) were activated, prior to use, at 105°C for one hour.

Part (80%) of the purified radiochemical of specific activity 2.29 GBq/mmol (4.49×10^8 dpm/mg), unlabelled pirimiphos-methyl

and emulsifier supplied by ICI Ltd., were dissolved in distilled water to give a formulated material. Forty potatoes of approximate weight of 4 kg were cleaned from adhering soil and were treated with the prepared formulated material using a Burkard microapplicator. A volume (0.1 ml) of the formulated material (10 mg of 50 EC per ml) was applied per potato. Controls were similarly treated without the labelled material. Potatoes were stored at room temperature in double carton boxes which had been perforated for aeration. The monthly mean temperatures outside the store were the following: February 11°C, March 13.5°C, April 17°C, May 22°C and June 26°C.

The following procedure (Atreya and Upton 1983) was followed with some adjustments. Three treated potatoes and one control were analysed separately for residues in the skin and flesh. The skin and flesh were chopped in small pieces. The whole skin and 50g of flesh were macerated separately for 10 minutes in Waring blender with 20% acetone in hexane (150ml); the jar was kept cool by tap water to avoid possible degradation of residues. The homogenate was filtered and the procedure was repeated using solvent (100 ml). The filtered fractions were combined.

The filtrate was transferred to a separating funnel and distilled water (150 ml) was added. After shaking for two minutes the aqueous phase and any interfacial material were discarded. The hexane extracts were made to volume (300 ml) with hexane. Aliquot extracts of the skin (5 ml) and of the flesh (50 ml) were evaporated and radioactivity was measured (Step 1). Further, hexane aliquots of the skin (30 ml) and flesh (100 ml) were extracted with acetonitrile (2x80 ml). This extract was evaporated to a volume (30 ml) and transferred to the separating funnel. A 5% Na_2SO_4 solution (100 ml) was added and residues extracted with hexane (2x100 ml). The hexane extract was dried by anhydrous Na_2SO_4, evaporated to a 2-3 ml and added to a deactivated Florisil column. Pirimiphos-methyl was eluted with 150 ml n-hexane + diethyl ether (7 + 3), and eluent evaporated to dryness. The residue was dissolved in acetone (5 ml) and an aliquot (1 ml) was used for radiocounting (Step 2). Subsequently, the Florisil column was eluted (100 ml) with diethyl ether + acetone (9 + 1) to identify any metabolites. The rest (4 ml) and metabolite eluents were applied on TLC plates and eluted with chloroform methanol (195 + 5). The spots were detected under UV light and autoradiography using Kodak SB film and then counted (Step 3). An LKB rackbeta scintillation counter model 1211 was used for measurement of radioactivity.

RESULTS AND DISCUSSION

Similar results were obtained for steps I and II and decay curves are shown in Figures 1 and 2. TLC analysis showed that the residues present in the potato skin were composed of the

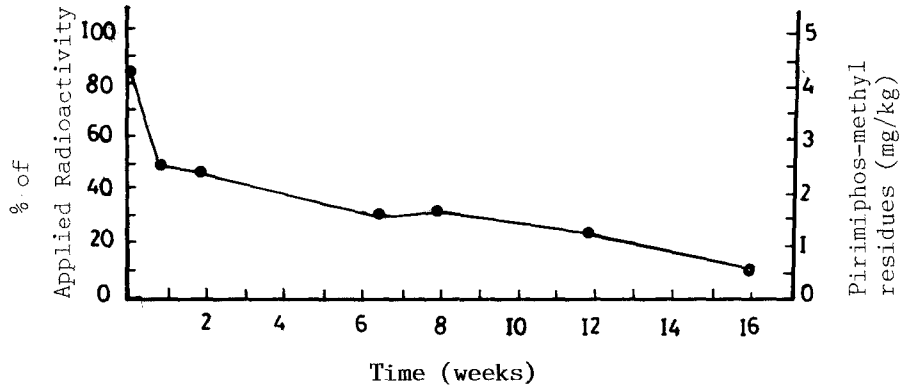

Figure 1. Pirimiphos-methyl residues in potato skin. Each point is the mean value for the analysis of three samples

parent compound (Rf=0.67) and traces of metabolites which constituted approximately to 7% of the residues in the skin. One metabolite had an Rf=0.5 in the n-hexane + diethyl ether (7 + 3) eluent of Florisil and two metabolites (Rf=0.51 and 0.43) at the subsequent elution (100 ml) of Florisil with diethyl ether + acetone (9 + 1). These degradation products could not be identified because reference chemicals were unavailable. In the potato flesh only the parent compound was present. Previous work (Leahy and Curl 1982) showed that wheat and rice contained 2-diethylamino-4-hydroxy-6-methylpyrimidine residues at a level which ranged from 2.5 - 22% of the parent compound and traces of desethyl pirimiphos-methyl.

Figure 1 shows the percentage degradation of the applied labelled pirimiphos-methyl and its residues in the skin. The decay on the first week was rapid. This was due to volatilization and metabolic transformations in the skin. After the 8th day the degradation was slower indicating that the main route of decay was volatilization. The increase in the mean temperature from 13.5^{o}C in February to 26^{o}C in June contributed to a large extend to the decay. Some insignificant penetration of pirimiphos-methyl existed in the flesh. This fact can be seen in Table 1 and results of autoradiography where pirimiphos-methyl in the flesh constituted to a small percentage (0.5%) and metabolites were absent. Figure 2 shows that pirimiphos-methyl exhibits typical residue dissipation pattern. Its residues degradated to 10% of the initial application in 16 weeks. In Nigeria, maize stored outdoors in the crib lost 70% of its initial deposition by the end of the 5th month and when stored indoors dissipated to 50% in 12 months (Sowumi and Fetuga 1983).

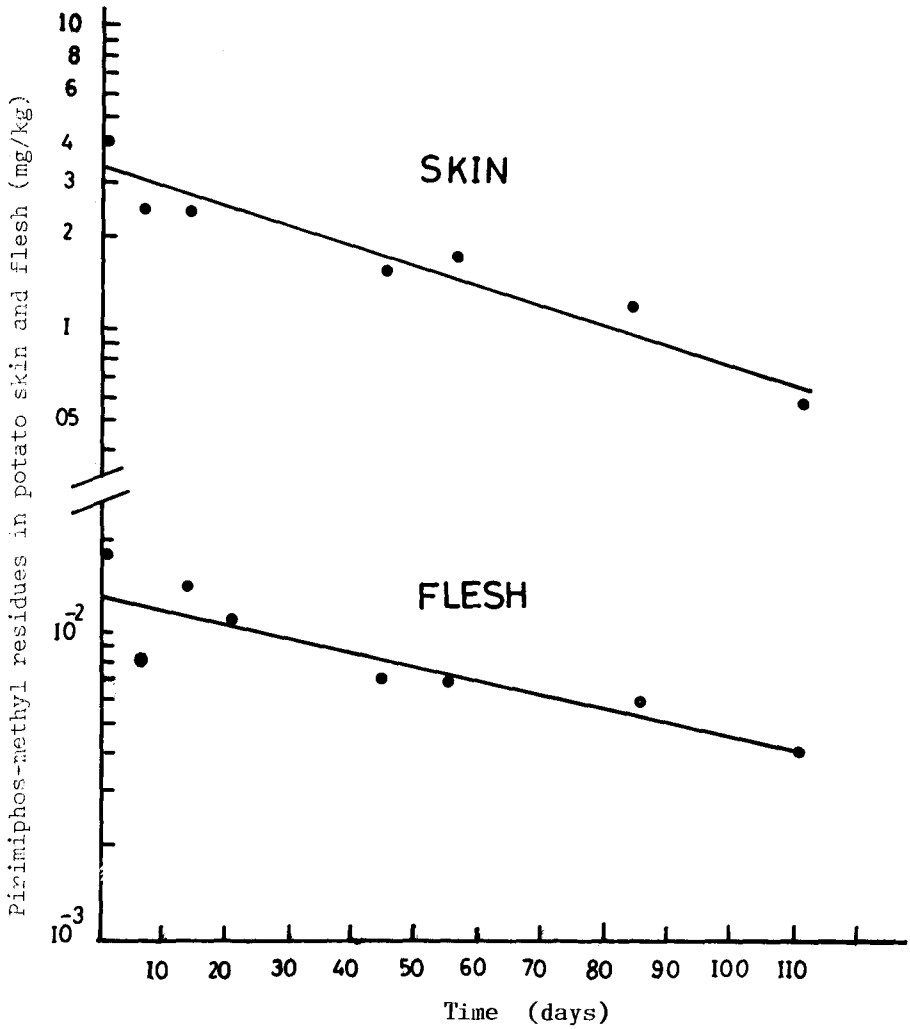

Figure 2. Pirimiphos-methyl residues in potato skin and flesh. Each point is the mean value for the analysis of three samples.

Apparent half-life values for pirimiphos-methyl residues were calculated to be 47 (r=0.956) days for the potato skin and 64 (r=0.881) days for the potato flesh. These values were lower than that of wheat grain (43 weeks) (Leahy and Curl 1982).

The residues of pirimiphos-methyl calculated from radioactivity results show that these residues are mainly found on and in the skin (99.5%), whereas in the flesh only a minimal part was traced (0.5%)(Table 1).The maximum residue limit(MRL) of

pirimiphos-methyl in potatoes established by FAO/WHO is 0.05 mg/kg (Anonymous 1984) which is far below the results found for the skin. The residues found in the flesh are below the MRL level. Results from the potato skin and flesh were calculated for the whole potato and it was found that residues were consistently above the MRL (Table 1).

Table 1. Residues of pirimiphos-methyl in potato skin and flesh

Storage time (days)	Skin		Flesh		Whole Potato
	mg/kg	%	mg/kg	%	mg/kg
1 (Feb.26)	4.22	99.6	0.018	0.4	1.07
7	2.49	99.7	0.008	0.3	0.63
14	2.42	99.5	0.014	0.5	0.62
21	N.D	N.D	0.011	N.D	N.D
45	1.58	99.6	0.007	0.4	0.40
56	1.72	99.6	0.007	0.4	0.44
84	1.19	99.5	0.006	0.5	0.30
111	0.55	99.3	0.004	0.7	0.14

N.D. Not determined

It can be concluded that the residues of pirimiphos-methyl on the skin constitute the major part of the total residue (> 99%). Humans consuming potato (excluding skin) are unlikely to run any risk of exposure to the chemical.

Acknowledgments. The author gratefully acknowledges the technical assistance of Mrs. Stella Kourtellari and Mr. K. Kyriakides. Financial assistance was provided by the Food and Agricultural Organization and the International Atomic Energy Agency.

REFERENCES

Ali AUDD (1974/1976) Susceptibility tests of tuber moth Phthorimaea operculella Zeller to chemicals and Thuricide-HP. Yearbook of Plant Protection Research, Iraq 1: 54-59

Anonymous (1977) Bibliography on pirimphos-methyl. ICI Plant Protection Division, Surrey

Anonymous (1984) Guideline levels for pesticide residues. Codex Alimentarious Commission FAO/WHO, Rome, Part 3: 55-56

Atreya NC, Upton BP (1983) Analytical method No. 11/B. ICI Plant Protection Division, Surrey

Leahy JP, Curl EA (1982) The degradation of pirimiphos-methyl on stored grains. Pestic Sci 13: 467-474

Morris HM (1983) Potato tuber moth. Cyprus Agr J 28: 111-115

Sowumi OE, Fetuga BL (1983) The degradation of pirimiphos-methyl applied to stored yellow maize in the hot humid tropics. Bull Grain Technol 21 (2): 105-109

Received August 8, 1986; accepted June 11, 1987.