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Residues of Malathion in Stored Grains

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The insecticide malathion (S-[1,2-bis(ethoxyzarbonyl)ethyl] O,O-dimethyl phosphorodithioate) is used for the control of pests in stored grains. The insecticide has a low mammalian toxicity and it can be mixed directly with the grains (Rowlands and Horler 1967). Malathion is widely used to control pests in stored maize, beans, wheat and barley in Turkey. It is applied at a rate of 500 g of 2% malathion dust per tonne of grains which is equivalent to 10 ppm of active ingredient. This paper reports on the levels of ^{14}C-residues remaining in maize, beans, wheat and barley treated with ^{14}C-malathion and stored for nine months under central Anatolian conditions. Enamelware buckets were used for storage in order to simulate the local conditions. The effect of cooking and/or baking of grains after storage on the distribution of ^{14}C-residues was also determined.

MATERIALS AND METHODS

^{14}C-Malathion with a specific activity of 37 mCi/mmol was purchased from Armersham International Limited, UK. Nonradioactive malathion was obtained from the Plant Protection Institute in Ankara. All reagents used were of analytical grade. The scintillation cocktail was prepared by dissolving 7 g of PPO, 0.05 g of POPOP and 50 g of naphtalene in 1 liter of dioxane.

Samples of maize, beans, wheat and barley that had never been treated before with any pesticide were obtained from the Plant Protection Institute in Ankara for this investigation. Analysis of these samples, as described later, indicated that they were free of malathion and/or metabolite residues. Cracked seeds and foreign materials that might affect residue levels were removed by hand (Anderegg and Madisen 1983). The moisture content of the grain was determined by weighing and oven drying 10 g of the seeds for 18 h, at 130 °C. Quantities of 1.5 kg of each sample were treated with 137 μCi ^{14}C-malathion + 0.75 g of 2% nonradioactive malathion dust to give a final concentration of 10 ppm active ingredient. Treated grain samples were stored in enamelware buckets at ambient temperature of 10-30 °C. At these levels no growth of pests and/or other microorganisms was observed during storage.

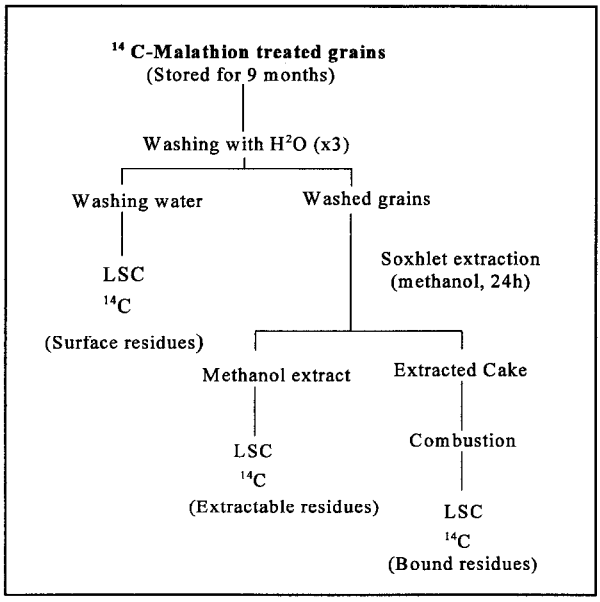

Figure 1. Schematic diagram for ^{14}C residue analysis

At the end of nine months samples of ^{14}C malathion treated maize, bean, wheat and barley were processed as shown in Figures 1 and 2. All samples were analysed in triplicate for ^{14}C analysis.

(I) Surface ^{14}C-residues. A 50 g sample of stored grain was washed 4 times with 50 ml of distilled water to remove the surface residues. An aliquot (1 ml) was taken from each wash and counted in a liquid scintillation counter (LSC). (ii) Extractable ^{14}C-residues. The washed sample was ground thoroughly and transferred to a thimble of a Soxhlet apparatus. The sample was subjected to Soxhlet extraction with methanol for 24 h. After the completion of the extraction, the volume of the extract was measured and an aliquot (2 ml) was radioassayed. (iii) Nonextractable (bound) ^{14}C-residues. The unextracted ^{14}C-residues in maize, beans, wheat and barley were determined by the combustion of approximately 200 mg of material that was dried at room temperature after the extraction. The combustion process was carried out in Packard Tri Carb B 306 sample oxidizer and the radioactivity counted by an LSC.

The cooking and baking processes were performed on samples after nine months of storage. The procedure for baking of maize, wheat and barley, and cooking for maize and beans is shown in Figure 2.

RESULTS AND DISCUSSION

The ^{14}C-residues on the surface of grain seeds removed by washing with water are shown in Figure 3. It was observed that after 9 months of storage beans retained the

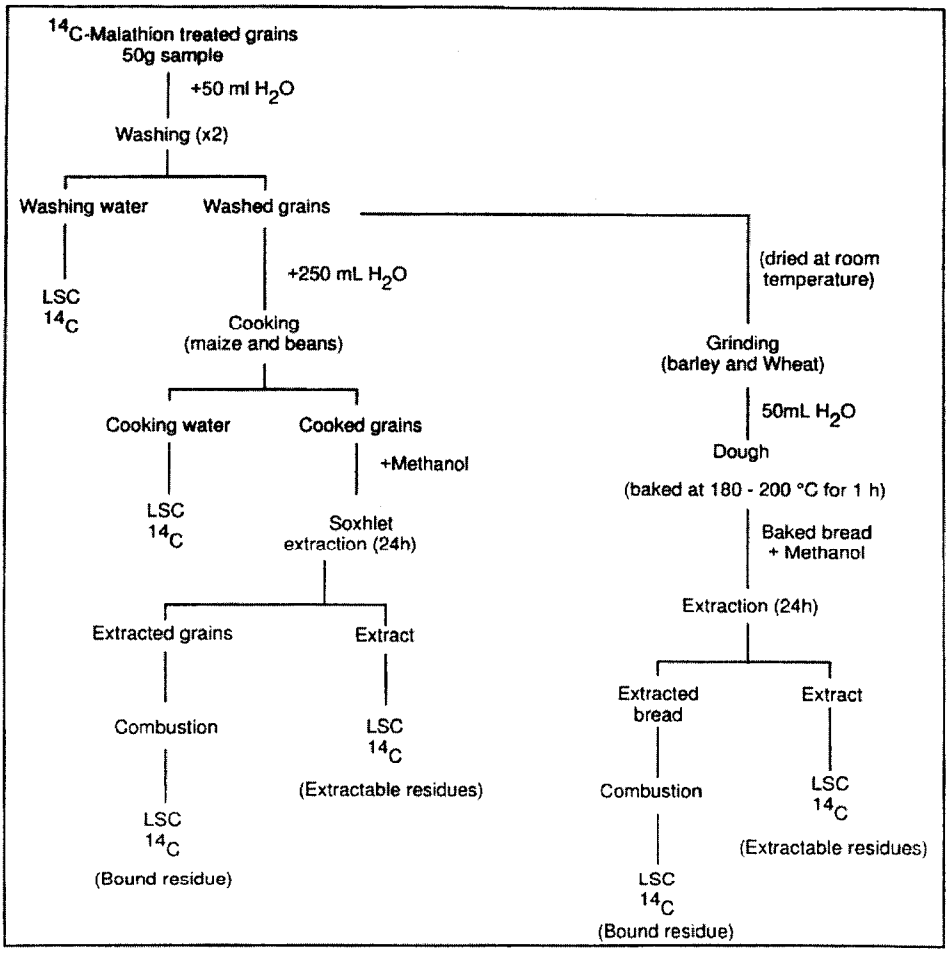

Figure 2. Cooking and baking procedures for grains.

highest amount of surface ^{14}C-residues followed by maize, wheat and barley. The amounts of methanol extractable ^{14}C residues in beans were relatively very low compared to those found in the other grain samples studied. These observations suggest that in beans very little defusion of ^{14}C-malathion occurred during the 9 months storage period whereas maize, wheat and barley absorbed relatively higher amounts of ^{14}C residues. Figure 3 also illustrate the total amounts of ^{14}C-residues present in each grain samples under investigation. These values ranged equivalent to 5.3 to 5.7 ppm of the insecticide which are below the maximum residue limits (FAO/WHO 1979).

From a practical point of view washing of beans with water appears to be very desirable practice as this will remove residues of the insecticide in the grains stored for an extended period of time.

Table 1. ^{14}C -residues in stored maize and beans after cooking

TYPE OF GRAIN	COOKING WATER	EXTRACTABLE RESIDUES	BOUND RESIDUES	TOTAL ^{14}C-RESIDUES
	% ^{14}C of the initially applied			
Maize	8.6	16.7	3.7	29.7
Beans	7.0	9.8	4.1	20.9

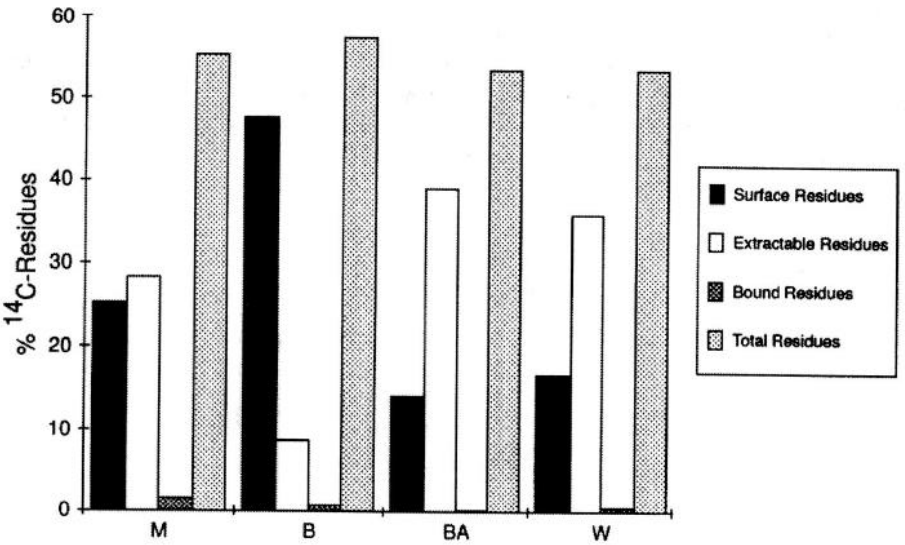

Figure 3. Distribution of ^{14}C-residues in ^{14}C-malathion treated maize (M), beans (B), barley (BA) and wheat (W) after 9 months of storage.

Table 1 shows the effect of cooking on the distribution of ^{14}C in beans and maize. The normal practice involves only one washing with water of beans prior to cooking. However, even though in our study we washed beans twice with water, it apparently did not remove all the surface adsorbed ^{14}C material (Table 1). It was observed that nonextractable (bound) ^{14}C-residues substantially increased after cooking, presumably owing to easier penetrations into the softened grains.

The total ^{14}C-residues after the baking process in barley and wheat were 36.0 and 27.0 % of the unbaked grains, respectively. About 14-17 % ^{14}C-residues of the initially applied ^{14}C were removed by washing barley and wheat before baking

(Figure 2, Table 1). The latter process appears to result in a decrease of total ^{14}C-residues. Thus, the total extractable and bound ^{14}C-residues in barley and wheat (after washing) amounting to 39.5 and 37.0 % were decreased after baking to 36.0 and 27.0 %, respectively. The overall results suggest that washing of stored grains is a very desirable practice in order to remove a substantial part of the insecticide residues before cooking or baking.

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