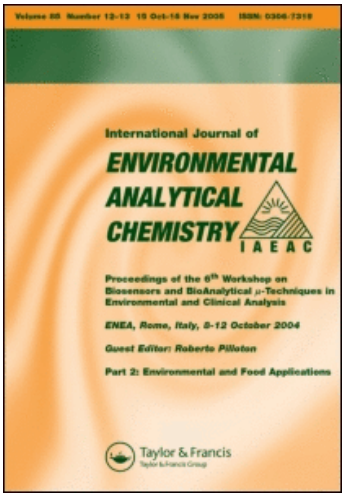

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N. Kannan[a]; J. Jayaraman[a]; R. Janarthanan[b]; S. Sridharan[b]
[a] Department of Biochemistry, School of Biological Sciences, Madurai Kamaraj University, Madurai, India [b] Department of Entomology, Agricultural College and Research Institute, Madurai, India

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Disappearance of Dislodgable Residues of Methomyl from Leaves and Vegetables in Tamilnadu (India)

N. KANNAN and J. JAYARAMAN†

Department of Biochemistry, School of Biological Sciences, Madurai Kamaraj University, Madurai 625 021, India

and

R. JANARTHANAN and S. SRIDHARAN

Department of Entomology, Agricultural College and Research Institute, Madurai 625 104, India

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The dislodgable residues of methomyl from leaves and vegtables were determined by a single-step methanol extraction followed by reversed-phase HPLC. The residues on the bhendi vegetables and leaves were several times higher than on the brinjal vegetables and leaves. The pesticide, however, dissipates rapidly under the South Indian climatic conditions resulting in undetectable residues within three days of spraying.

KEY WORDS: Dislodgable residues of methomyl, HPLC method, low residual life on semi-tropics.

†To whom correspondence should be addressed.

INTRODUCTION

Worker-environment research in agricultural fields has not picked up momentum in India. Once insecticides are sprayed onto crops, the residual amounts on the surface of leaves, vegetables and fruits pose a health hazard to the farmers re-entering the fields for other agricultural operations. Dermal contact and inhalation of vapours are the major routes through which the toxic chemicals enter the human system. With the average Indian farmer generally being half naked and working under the hot tropical sun, volatilisation of the insecticides is also a major problem. We have recently initiated studies to investigate the dislodgable residues on the surface of leaves and vegetables. Results obtained in brinjal (*Solanum melongena* L., common name egg plant) and bhendi (*Abelmoschus esculentus* L. Moench) after spraying with methomyl, are reported in this paper.

Methomyl (S-methyl-N-(methyl carbamyl)-oxythioacetimidate) is a broad-spectrum insecticide and acaricide with some nematocidal properties. It is an effective agent against lepidopterous larvae and aphids and is recommended for vegetables. It has been recently introduced in India. It has been shown that methomyl is absorbed by dermal contact and by inhalation, and is highly toxic in the latter route.[1] The nitroso derivatives of methomyl, which are easily produced under the low pH conditions in the stomach, were found to be mutagenic to procaryotes[2] and to *Salmonella typhimurium* TA 1535.[3]

High-performance liquid chromatography (HPLC) has been successfully used by several workers to estimate methomyl residues in various plant materials.[4-8] In our experiments, we have used reversed-phase HPLC with UV detection at 254 nm.

METHODS AND MATERIALS

The plants were grown in plots of 10 m^2. Lannate 24L, a commercial formulation of methomyl, was applied as foliar spray, using a high-volume hand-operated sprayer. Two concentrations, the standard 0.45 kg active ingredient (ai)/ha and a higher dosage of 0.75 kg ai/ha, were used. Three plots accommodated in random block design were used for each dose. The first spraying was applied when the plants were 30 days old, in order to control sucking pests, the second and

subsequent sprays at 15-day intervals to control fruit borers (such as *Erias* sp. on bhendi and *Leucinodes orbonalis* in brinjal), following the local agrarian practice. During the second spraying with the above-mentioned dosages, samples were taken. Within this period the workers are active in the field, picking fruits. Vegetables and leaf samples of brinjal were taken 3 h, 4 days and 7 days after spraying and bhendi samples were taken 3 h, 3 days and 5 days after spraying. Samples of ten vegetables and ten leaves were randomly collected in glass beakers and transported to the laboratory for immediate analysis. Control samples were also collected in the same way.

During the test period (August 10–17, 1984), the maximum and minimum air temperatures were 36.5°C and 26.2°C, respectively, and the maximum and minimum humidity were 55% and 28.41%, respectively. There was no precipitation during the period.

The collected samples were thoroughly washed with 100 ml distilled methanol in 500 ml glass beakers. The extract was filtered, then concentrated to 5 ml *in vacuo*.

The HPLC system used to determine methomyl has been extensively described earlier.[9] Methanol–water (70:30, v/v), used as mobile phase, was degassed by sonication before use. Standard solutions of methomyl (crystalline analytical standard supplied by Coromandel Indag, India) were prepared freshly at a concentration of 1 mg/ml methanol. Using a flow-rate of 0.5 ml/min, methomyl had a retention time of 6.15 min. Under these conditions the detection limit was 1 μg. As Figure 1 shows, no interfering peaks were present in the control samples. Quantification was done by integration of peak area, using the external standard method.

RESULTS AND DISCUSSION

Extraction of methomyl residues from the surface of vegetables and leaves was carried out with methanol at room temperature (about 30°C). Experiments with spiked samples resulted in more than 90% recovery of methomyl from the leaves. In the case of whole vegetables recovery was higher than 80%. The sensitivity of the method was 0.01 ppm, based on 100 g wet weight of sample. The method could be readily applied for routine monitoring purposes. The tolerance limit of methomyl in vegetables established by the

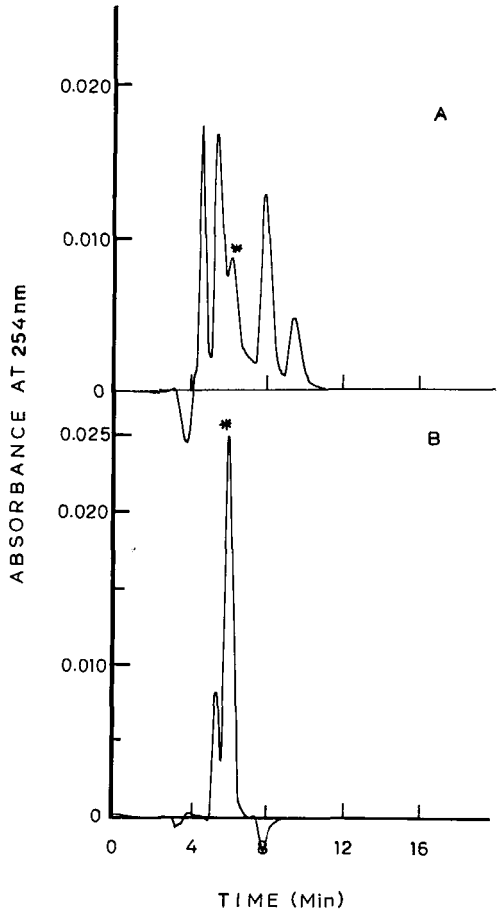

FIGURE 1 Reversed-phase HPLC of methomyl (see asterisk) in vegetables. (A) A representative chromatogram of methomyl-treated bhendi leaf extract. This corresponds to the zero day sample of bhendi in Table I giving a value of 6.48 ppm. Spiked samples confirm identification of peak. (B) Methomyl technical standard. 10 μl injection (10 μg). The smaller peak is an impurity in methanol.

Environmental Protection Agency (U.S.A.) is 0.2 ppm. Extraction with hot methanol (60°C) did not improve the recovery. Because the method involves only surface washing for the estimation of dislodgable residues, the extensive solvent partitioning used by Alawi and Ruessel[7] and Thean *et al.*[6] is not needed. This not only simplified

the procedure but also resulted in recoveries higher than those obtained by the method of Thean *et al.*,[6] in which methomyl residues were trapped in the lipid micelles occurring in vegetable extracts. The sensitivity of our procedure is less than that reported by Alawi and Ruessel,[7] who used UV detection at 233 nm instead of 254 nm as used by us.

The results of the experiments are presented in Tables I and II. The foliar residues are expressed in $\mu g/cm^2$ of leaf (one side only). The residues were only detectable on the day of spraying: 6.48 $\mu g/cm^2$ on the leaves of bhendi as compared to 2.03 $\mu g/cm^2$ on brinjal plant leaves. It is encouraging to note that dislodgable residues on leaves were undetectable on subsequent pickings. It has been reported by Cahill *et al.*[10] that methomyl disappears rapidly from cotton leaves: less than 1% deposit value was found on the fourth day (see also Ware *et al.*[11]). When the pesticide was sprayed on rape plant, at a dose of 85 ml/acre, the initial deposit of 17 ppm decreased to 1 ppm after 1 day of spraying and to 0.2 ppm on the ninth day.[12]

A similar situation is obtained with the vegetables. The initial deposits are rather high (Table II) but already on the third day after spraying, they are below the detection limit. The initial deposit in the bhendi is several times higher than brinjal. The skin of bhendi is hairy and the vegetables project out, whereas the skin of brinjal is shiny and the vegetables are usually shaded under the thick canopy of leaves. Similar observations have been made on celery by Harris *et al.*[13] with a 75% reduction of the residue level within seven days. Field efficacy studies, conducted along with the above residue studies, support our findings of the fast disappearance of the pesticide under our experimental conditions.[14]

The minimal "re-entry period" of three days suggested by us earlier, for rice plants and tomato,[15,16] has to be stressed again for farmer safety.

The current study was initiated to develop a simple and fast method for the determination of the dislodgable residues as part of worker–environment research and hence a method of pooling composite samples was adopted rather than the elaborate procedure of individual triplicates; such data are acceptable.[17] There exists a controversy regarding the use of organic solvents to extract the dislodgable residues[18] based on the idea that the dislodgable residues are strictly superficial and should be removed by water

TABLE I

Dislodgable residues of methomyl on leaves (one surface only).

Crop	Dosage (kg ai/ha)	Interval between treatment and sampling (days)	Residue[a] (mg/kg)
Brinjal	0.75	0	2.03
		4	BDL[b]
		7	BDL
Bhendi	0.75	0	6.48
		3	BDL
		5	BDL

[a]Residue values were obtained after washing ten leaves with methanol.
[b]BDL—below detection limit.

TABLE II

Dislodgable residues of methomyl on vegetable surface.

Crop	Dosage (kg ai/ha)	Interval between treatment and sampling (days)	Residue[a] (mg/kg)
Brinjal	0.45	0	5.04
		4	BDL[b]
		7	BDL
	0.75	0	6.05
		4	BDL
		7	BDL
Bhendi	0.45	0	21.23
		3	BDL
		5	BDL
	0.75	0	42.91
		3	BDL
		5	BDL

[a]Residue values were obtained after washing ten fruits with methanol.
[b]BDL—below detection limit.

washing. However, we adhere to the view of Cahill *et al.*[10] who use organic solvents, assuming that the dislodgable residue is probably greater than just surface residues, as evidenced by the larger deposits of chlorophyll on the clothing and hands of individuals after working in the field.

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