

INSECTICIDE RESIDUES IN VEGETABLES

II. EFFECT OF DOSAGE RATES AND PREHARVEST INTERVALS ON RESIDUES IN AND ON GREEN BEANS (*Phaseolus vulgaris* L.)¹

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The effect of application rate and preharvest intervals on residue levels of some organophosphorus insecticides in green beans (*Phaseolus vulgaris* L.) was determined. A rapid decline in residue levels in or on the pods was observed. No residues could be detected 5 days after application.

The organophosphate insecticides are currently the most used insecticide group for crop protection and vegetable production is no exception. While they are generally less persistent than their predecessors, the organochlorine insecticides, they could also leave residues in treated crops. This problem is all the more pronounced with vegetables because they constitute a significant source of the Filipino's protein intake.

In addition, residue data under tropical conditions have been generally lacking or unavailable for international evaluation as a basis for setting maximum residue limits (MRL) acceptable in international trade (FAO 1978). This absence of a data base caused most scientists to assume that because of the more intense environmental factors in the tropics, residue degradation must be more rapid than in temperate areas. Therefore, if MRL is based on data from temperate regions, it is not expected to be exceeded in the tropics when the same insecticide is used on the same crop, following the same agricultural practice. This assumption is generally considered valid but then it works on the assumption that the crop protection practices precipitated by differing pest problems, are identical. It is therefore still important to conduct residue analysis work in tropical countries, simulating actual use conditions and in line with established priority activities.

This work is part of a continuing program to pinpoint practices which could lead to the reduction in insecticide residue levels in different vegetables. The practice would then be incorporated into a pesticide management package for possible adoption by farmers (Magallona, 1978). Green beans (*Phaseolus vulgaris*), commonly known as pole sitao, was selected because it is a widely consumed vegetable of high nutritive value. Total protein content is as high as 20-25 percent and carbohydrate is about 50 percent. In the Philippines, it is generally grown in the low elevation areas and marketed

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fresh in the urban centers. The insecticides chosen for this study are among the more widely marketed and popular compounds. While the crop protection practices of green beans producers are very variable, the intense insecticide application regime used in this study could form the basis of recommendations during heavy infestations which could still result in safe residue levels; less intense application regimes would naturally result in lower residues.

MATERIALS AND METHODS

Field Experiment. Green beans (*Phaseolus vulgaris* L.) were planted at the Central Experiment Station, UP at Los Baños, on January 26, 1978 using a randomized complete block design replicated twice. Each treatment consisted of about 20 plants. Insecticide application was done weekly starting one week after germination for a total of eight applications with the following insecticides and application rates.

Experiment I

Treatment	Formulation	Rate	%
Methyl parathion	Unidol 50%	2.5 tsp/11.5 L	0.05
Methyl parathion	Unidol 50%	5 tsp/11.5 L	0.10
Monocrotophos	Azodrin 202 R	3 tbsp/19 L	0.05
Monocrotophos	Azodrin 202 R	6 tbsp/19 L	0.10

Experiment II

Methyl parathion	Unidol 50%	2.5 tsp/11.5 L	0.05
Mevinphos	Phosdrin 1.5 EC	3 tbsp/19 L	0.002
Monocrotophos	Azodrin 202 R	3 tbsp/19 L	0.05
Tetrachlorvinphos	Gardona 75 WP	4 tbsp/19 L	0.15
Triazophos	Hostathion 40%	1 tbsp/19 L	0.02

Field Sampling. Last spraying was done on the 48th day after planting and the first random samples were harvested three hours after spraying, just allowing the plant surface to dry. Further samples were taken at different intervals up to the seven days after last application. In each case, 0.5 kg samples were taken per treatment per sampling.

Laboratory Sampling. The field samples were chopped into smaller pieces and three 25 g representative samples were wrapped in aluminum foil for storage in a freezer at -21°C until analysis.

Extraction. After thawing, the sample was blended with seventy five ml of acetone. The mixture was filtered and the filtrate was partitioned using a 1:1 solution of methylene chloride and petroleum ether. The bottom layer was transferred to another separatory funnel, 10 ml of saturated sod-

ium chloride was added and the solution was partitioned twice with 50 ml of methylene chloride. The organic extracts were combined and passed through anhydrous sodium sulfate into a 250 ml round bottom flask. The organic solvent was then evaporated in a rotary evaporator and the residue was dissolved in two ml of glass distilled hexane for gas chromatography.

Gas Chromatography. A Varian 1400 Gas Chromatograph equipped with an alkali flame ionization detector was used with the following parameters:

Column	:	3' x 1/8" O.D. Stainless Steel packed with 5% DC 200 on 80/100 Gas Chrom Q.
Temperatures (°C)	:	Column 200
	:	Detector 230
	:	Injector 250
Flow rates (ml/min)	:	Nitrogen 21
	:	Hydrogen 38
	:	Compressed Air to 200
Retention Times (min)	:	Methyl parathion 2.4
	:	Mevinphos 0.6
	:	Monocrotophos 1.6
	:	Tetrachlorvinphos 3.7
	:	Triazophos 6.1

Quantitation was based on peak height. To compensate for changes in sensitivity with time, an alternate injection sequence of standard and sample was made. The chromatograms for each insecticide are shown in Figures 1-5.

RESULTS AND DISCUSSIONS

Recovery studies at the 0.1 ppm fortification levels showed recoveries in the 78-110 percent range and detection limits of 0.01 mg/kg for methyl parathion, 0.02 mg/kg for mevinphos, and 0.05 mg/kg for monocrotophos, tetrachlorvinphos, and triazophos (Table 1). These detection limits are adequate if considered against the MRLs or tolerances given in Table 2. During the last spraying up to harvesting, the meteorological conditions are as summarized in Table 3.

From Table 4 it is seen that although the use of double the recommended concentrations of methyl parathion and monocrotophos resulted in higher initial residue levels, the loss rate was also faster. Thus, for both spray concentrations, there were no detectable residues five days after last application.

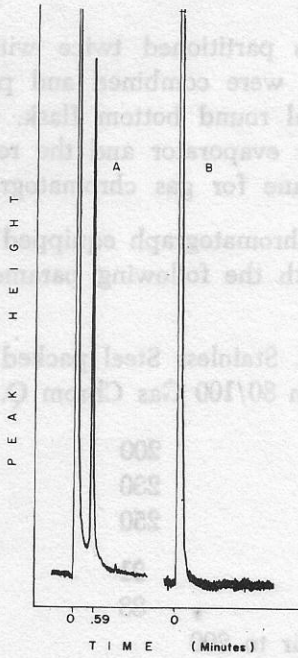


Fig. 1. Gas Chromatogram of A) Mevinphos standard B) Green beans sprayed with mevinphos

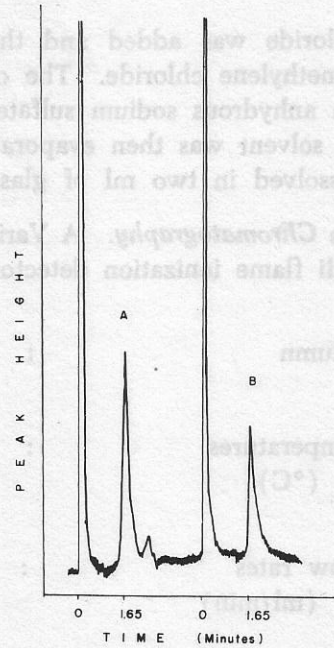


Fig. 2. Gas Chromatogram of A) Green beans sprayed with monocrotophos B) Monocrotophos standard

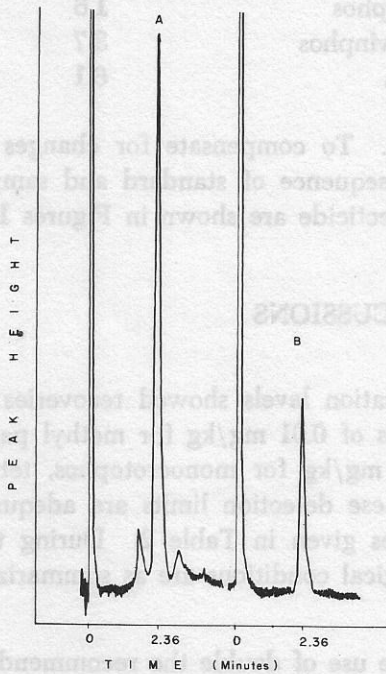


Fig. 3. Gas chromatogram of A) Green beans treated with methyl parathion B) methyl parathion

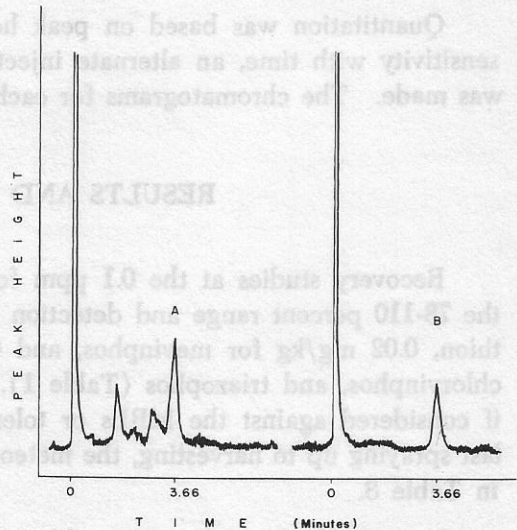


Fig. 4. Gas Chromatogram of A) Green beans treated with tetrachlorvinphos B) tetrachlorvinphos standard

TABLE 1. Recovery of some organophosphorus insecticides in green beans

Insecticides	Recovery %	Limit of Detection (mg/kg)
Methyl parathion	93	.01
Mevinphos	78	.02
Tetrachlorvinphos	110	.05
Triazophos	100	.05
Monocrotophos	80	.05

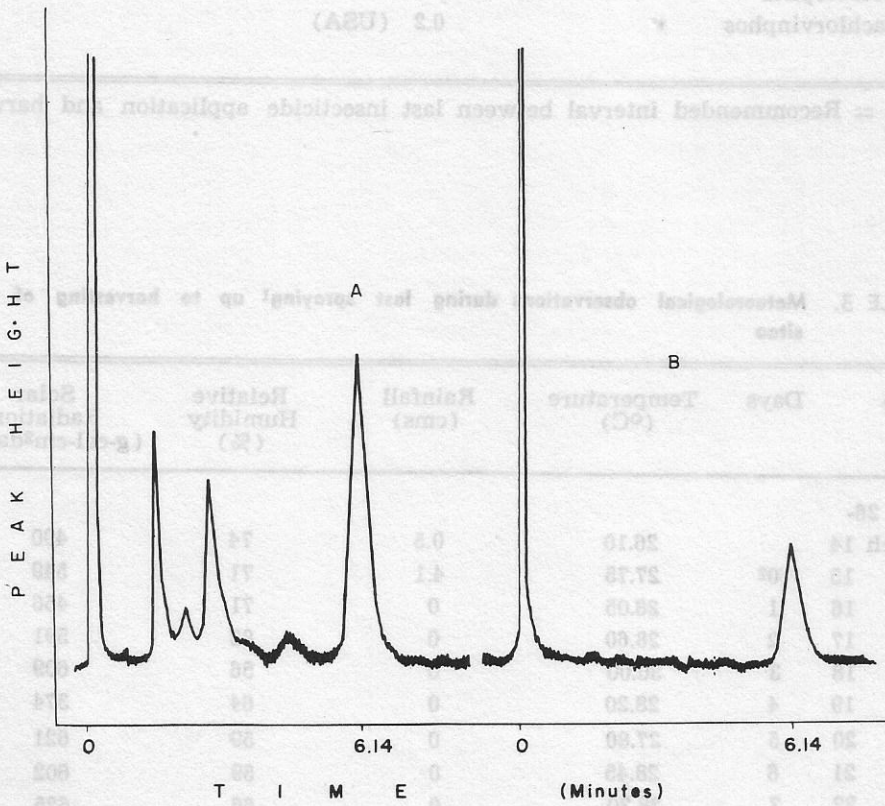


Fig. 5. Gas chromatogram of A) Green beans treated with triazophos B) Triazophos standard

TABLE 2. Maximum Residue Limits (MRL) and some tolerance for insecticide use in experiment

Insecticide	MRL (mg/kg)	Tolerance (mg/kg)	PHI (days)
Methyl parathion	1	0.15 (Germany)	24
		0.5 (Netherlands)	21
		1.0 (USA)	7-21
		1.0 (Australia)	21
Mevinphos	0.1	0.25 (USA)	1
		0.25 (Australia)	2
		0.25 (Canada)	1
		0.1 (Germany)	
		0.1 (Netherlands)	7
Monocrotophos	0.2		21
Tetrachlorvinphos		0.2 (USA)	

PHI = Recommended interval between last insecticide application and harvest.

TABLE 3. Meteorological observations during last spraying¹ up to harvesting of pole sitao

Date	Days	Temperature (°C)	Rainfall (cms)	Relative Humidity (%)	Solar Radiation (g-cal-cm ² day ⁻¹)
Jan. 26-					
March 14		26.10	0.5	74	490
Mar. 15	0 ²	27.75	4.1	71	549
	1	28.05	0	71	456
	2	28.60	0	82	591
	3	30.00	0	56	609
	4	28.20	0	64	374
	5	27.80	0	59	621
	6	28.45	0	59	602
	7	28.30	0	66	625

¹ There was a total of 7 spraying at weekly intervals prior to the last spraying

² Sampling 3 hours after last spraying

TABLE 4. Residues of methyl parathion and monocrotophos on field treated greenbeans at recommended rates and double recommended rates

Preharvest Interval	Methyl Parathion		Monocrotophos	
	.05%	0.10%	.05%	0.10%
3 hours	1.3	2.5	1.6	2.9
1 day	0.4	1.1	1.7	2.7
2	0.1	0.6	0.7	1.0
3	.02	.06	0.3	1.0
5	ND	ND	ND	ND
7	ND	ND	ND	ND

ND = Non-detected <.01 mg/kg <.05 mg/kg

TABLE 5. Residues of some organophosphorus insecticides on field treated green beans.

Preharvest Interval	Methyl Parathion	Monocrotophos	Tetrachlorvinphos	Triazophos
3 hours	0.3	1.7	1.2	1.9
1 day	0.7	1.9	0.2	0.7
2	0.1	1.1	ND	0.4
3	0.01	0.4	ND	ND
5	ND	ND	ND	ND
7	ND	ND	ND	ND

Mevinphos — No detectable residues even after only 3 hours

ND = None-detected (< 0.01 mg/kg for methyl parathion and < 0.05 mg/kg for tetrachlorvinphos, triazophos and monocrotophos)

The residue data in Table 5 for four insecticides show that they are all readily lost from the plant surface such that in all cases, no residues could be detected five days after last application. In the case of tetrachlorvinphos, no residues could be detected as early as two days after last application. Mevinphos residues cannot be detected as early as three hours after application.

Mevinphos residues in crops have been known to decrease rapidly, partly due to volatilization and partly due to degradation. Residues of mevinphos did not exceed 0.05 mg/kg when beans were treated with 0.5 kg/ha mevinphos and sampled two days later (FAO/WHO 1973). The principal degradation products are dimethyl phosphate and acetoacetic acid.

In the case of monocrotophos, only low level residues have been detected in crops following recommended rates. In beans, application of up to 0.5 kg/ha and preharvest interval of 21 days gave residues ranging from less than 0.01 mg/kg to 0.22 mg/kg (FAO/WHO 1973). The primary metabolic products are non-cholinesterase inhibiting and of low toxicity.

Methyl parathion is a broad spectrum insecticide. It is used mainly on cotton but usage in food crops include those on fruits and vegetables (FAO/WHO 1977). As one of the cheaper commodity insecticides, its use is always expected of farmers for a variety of pest problems. In cotton, three metabolites were found in the leaves and one was identified as the highly toxic methyl paraoxon (Coffin 1964, Shipp et al., 1963). In general, only small amounts of methyl paraoxon have been found (one to four percent) but at elevated temperatures and high humidity, Shipp et al. (1963) found that the total cotton residues after 72 hours consisted of 14.5 percent methyl parathion and 38.5 percent methyl paraoxon. However, the oxon is subject to rapid hydrolysis in and on the plant.

CONCLUSIONS

With the existing use pattern in the Philippines, green beans treated with methyl parathion, mevinphos, monocrotophos and tetrachlorvinphos gave residues within internationally accepted tolerance limits or maximum residue limits if a five days interval between last application and harvest is observed. If insecticide application close to harvest is considered necessary, mevinphos may be used with the residues being low within one day after application. Triazophos has not been reviewed by the FAO/WHO Joint Meeting of Experts on Pesticide Residues so that no MRLs could be quoted. Tolerances in other countries are also not known at this time. However, since there are no detectable residues two to three days after application, the five days interval may likewise be considered safe.

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