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MONITORING OF DISULFOTON (DISYSTON) AND PHORATE (THIMET) RESIDUES ON COTTON CROP AFTER GRANULAR APPLICATION*

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Residue levels of disulfoton and phorate and their insecticidally active metabolites were estimated in cotton plants after making applications of their granular formulations to the field crop at recommended dosages. From the result obtained it is evident that approximately one-third residues were present in the plant by the end of 6th week. This implies that the insecticides are capable of providing protection to cotton crop against pest attack for about two months.

INTRODUCTION

The application of granular pesticides is an effective as well as safer method for crop protection. This is specially important in the early growing stages when infestation from leaf-eating insect pests can be devastating. Systemic insecticides commonly used on cotton for this purpose are organophosphate esters. The residual life and effectiveness of some of these organophosphates is good for just the desired period of time. The two of these insecticides more commonly used on cotton are disulfoton (disyston) and phorate (thimet). The manufacturers of these insecticides have reported their effectiveness on cotton to last for about 3 months after application. We have investigated the persistence of these two insecticides on cotton under local environmental conditions. The results are presented here.

EXPERIMENTAL

Material

Reagents and Solvents. They were of AR quality: Chloroform BDH; sodium sulphate Merck; sodium chloride (Merck Florisil); BDH sodium metabisulphite.

Pesticide Analytical Standards. They were obtained from Environmental Protection Agency, USA.

(I) *Disulfoton (Disyston):* $C_8H_{19}O_2PS_3$ (*O,O* – diethyl S-2-ethyl thioethyl phosphorodithioate)

(i) Disulfoton Sulphoxide

(II) *Phorate:* $C_7\ H_{17}\ O_2\ P\ S_3$ (*O, O*-diethyl methyl thiomethyl phosphorodithioate)

(i) Phorate sulphoxide

(ii) Phorate sulphone

Apparatus :

(a) *Gas chromatography:* Pye Unicam 204 Gas Chromatograph; glass column of length 1M; internal dia 4 mm; column packed with 1.5% SP-2250/1.95%, SP-2401 on 100/120-mesh Supelcoport; carrier gas, nitrogen 45 ml/min.; Ni_{63} electron capture detector temperature, 250°; column temperature, 180°; injection temperature, 200°; attenuation, 256.

(b) *Chromatography column:* A glass column (18x400 mm) with a stopcock.

Analytical Procedure.

(a) *Extraction:* The cotton foliage was cut into small pieces and 50 g. of sample were weighed and macerated with 100 ml. of chloroform in a blender for about 3 min. The chloroform layer was filtered through a Buchner funnel containing 10 g of anhydrous sodium sulphate, then washed with half its volume with a saturated sodium chloride solution. The solvent was evaporated under vacuum on a rotary evaporator.

(b) *Clean-up* Florisil (R) was slurried with chloroform (10g a Florisil per 100g sample) and transferred to a chromatographic column. About 2" of anhydrous sodium sulphate was layered on top of the column followed by elution

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with more chloroform. When chloroform reached the level of sodium sulphate the extract was transferred quantitatively on the column. The rate of elution was adjusted to 60 drops per min. and the first 150 ml of the eluate were collected. The eluate was shaken with 100/ml of freshly prepared sodium meta bisulphite for 1 min. The chloroform extract was filtered on cotton plug with anhydrous sodium sulphate. The water layer was shaken with 100 ml of chloroform twice and the chloroform extracts were combined and concentrated by evaporation by means of a rotary evaporator. The residue was redissolved in hexane and transferred to a 10 ml volumetric flask, and analysed by GLC.

(c)*Pesticide standards used:* Following standard solutions were made in hexane for optimizing the GLC calibration:

Concentration

Pesticide reference standard	nanogram per microlitre hexane
(i) Disulfoton	10
(ii) Disulfoton sulphoxide	10
(iii) Phorate	10
(iv) Phorate sulphoxide	8
(v) Phorate sulphone	12

Gas Chromatographic analysis yielded the following data (Figs. 1–2). Table 1, 2 and 3.

Table 1: GC analysis of reference grades insecticides and their metabolic products

Product	Retention time	Peak height	Quantity
Disulfoton	2.55 min.	40.5 mm	4 ng
Disulfoton sulphoxide	9.10 min.	8.5 mm	4 ng
Phorate	2.50 min.	73.0 mm	5 ng
Phorate sulphone	9.05 min.	67.0 mm	6 ng
Phorate sulphoxide	10.05 min.	10.0 mm	4 ng

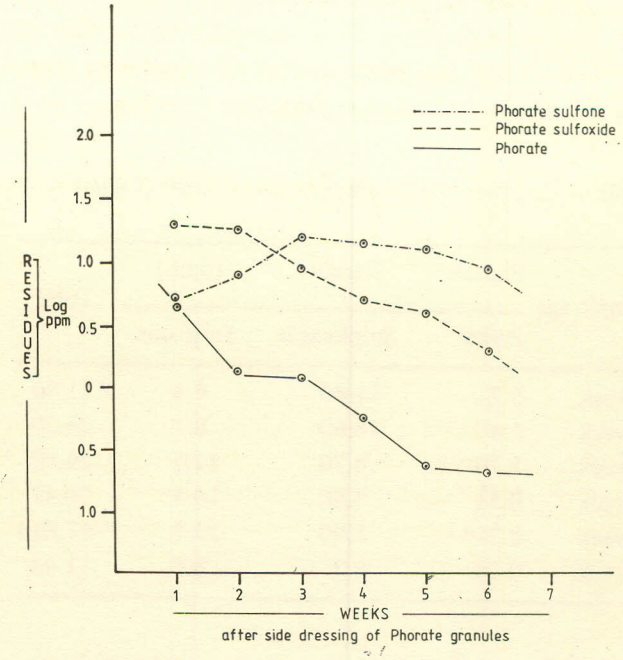

Fig. 1 The disappearance of phorate and its transformation products in cotton foliage.

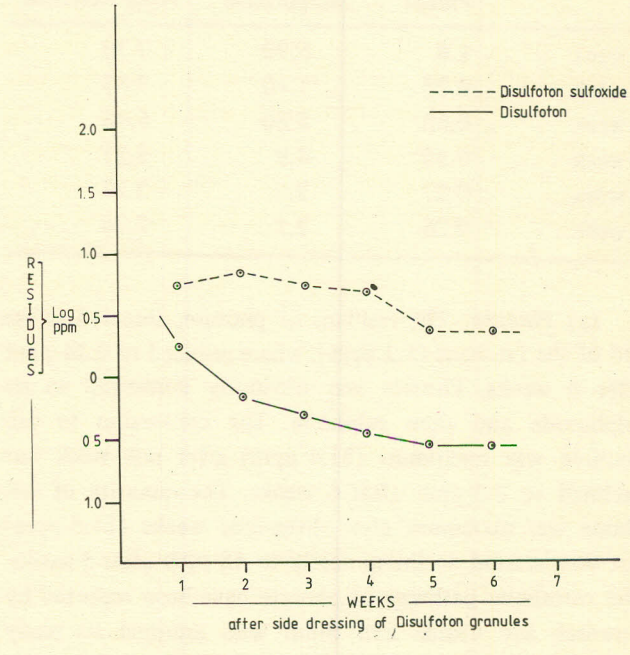

Fig. 2. The disappearance of disulfoton and its transformation products in cotton foliage.

RESULTS AND DISCUSSION

On the basis of the above calibration, residue levels were estimated from cotton extracts, as tabulated in (Table 2, 3).

The parent compounds appeared to be converted to their oxidation products. Total recoveries were higher in the cases of Phorate, about 3 times of Disulfoton. However in either case the residues dissipated with time.

Table 2: Residues of Phorate in cotton extract (foliar)

Sample age	Phorate Residue (ppm)			Total
	Parent	Sulphoxide	Sulphone	
1 week	5.2	21.40	4.8	31.40
2 week	1.4	18.60	8.7	28.70
3 week	1.20	8.70	14.5	24.40
4 week	0.51	5.40	14.5	20.41
5 week	0.214	3.90	13.7	17.814
6 week	0.24	2.3	8.9	11.44

Table 3: Residues of Disulfoton in cotton extract (foliar)

Sample age	Disulfoton Residues (ppm)		
	Parent	Sulphoxide	Total Residues
1 week	1.8	5.90	7.70
2 week	0.75	7.10	7.85
3 week	0.68	5.80	6.48
4 week	0.35	4.9	5.25
5 week	0.27	2.5	2.77
6 week	0.26	2.5	2.76

(a) *Phorate:* The residues of phorate, detected at the end of the 1st week (5.2 ppm), where reduced to 0.24 ppm after 6 weeks. Phorate was obviously converted to its sulphoxide and then sulphone. The conversion to sulphoxide was maximum (21.4 ppm) after one week but declined to 2.3 ppm after 6 weeks. The quantity of sulphone was maximum after three-four weeks (14.5 ppm) but then started declining nearly to 48 ppm after 5 weeks. The metabolic pathway of phorate have been reported by Bowman and Casida and Blinn who ascribed its ready conversion in plants, insects, and mammals to its oxidation products – Sulphone and sulphoxide as observed in these studies. The latter are insecticidally more active than the parent compound. These metabolites undergo further breakdown to various thio- and phosphoric acids and esters possessing no toxicological significance. American Cyanamid claimed that residues of phorate disappear between three weeks to three months. In Pakistan it is recommended that the first application of granular pesticides to cotton crop should be made with first irrigation to control insect pests which attack the crop in its early growing stages. Studies conducted by this laboratory indicate that nearly one-third amount of phorate, a great portion of it as sulphoxide and sulphone, was present in the crop at the end of 6th weeks of application, which implies that this insecticide is capable of providing protection to cotton crop for the initial and crucial period of about two months.

(b) *Disulphoton:* Disulphoton residues were gradually converted to its sulphoxide. After one week of application, 1.8 ppm residues of Disyston were detected which declined to 0.26 ppm after six weeks. On the other hand, 7.1 ppm sulphoxide was detected after 2 weeks which declined to 2.5 ppm after six weeks.

For disulphoton also, Metcalf, *et. al.* described a metabolic pathway similar to phorate, though a more rapid uptake in plants of the former was demonstrated, attributing it to the greater solubility of disulphoton in water. In the present studies, however, the conversion of disulphoton (parent compound) into sulphone could not be studied because of the non-availability of standard sample of this metabolite and we had to contain ourselves to studying conversion into sulphoxide only, which was available. Results obtained with this insecticide are comparable to phorate, providing the same clue, viz effective control of pests attacking cotton crop should be expected for a couple of months, if the application of this product is made with first irrigation. The disappearance of phorate and disulphoton is also being presented graphically.

REFERENCES

1. American Cynamid (USA).
2. J.S. Bowman, and J.E. Casida, J. Agr. Food Chem., 5, 192 (1975).
3. R.C. Blinn, J. Assoc. Off. Agr. Chem., 47, 641 (1964).
4. R.L. Metcalf, T.R. Eukute and R.B. Marsh, J. Econ. Ent., 50, 338 (1957).