THE GAS-CHROMATOGRAPHIC DETERMINATION OF ORGANOPHOSPHORUS PESTICIDES*

PART V. STUDIES UNDER FIELD CONDITIONS

J. H. RUZICKA, J. THOMSON AND B. B. WHEALS
Ministry of Technology, Laboratory of the Government Chemist, Cornwall House, Stamford Street, London, S.E. 1 (Great Britain)
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SUMMARY

In this paper the authors have studied the breakdown of the organophosphorus pesticides under growth conditions and compared the influence of irradiation and hydrolysis on the breakdown of this group of pesticides.

INTRODUCTION

The decay of organophosphorus pesticides sprayed onto crops is due to breakknown occurring primarily as a result of hydrolysis and irradiation. In previous papers we have described the use of gas chromatography in studying the breakdown of organophosphorus pesticides by hydrolysis[1] and ultra-violet irradiation[2] under laboratory conditions. The significance of results obtained in laboratory experiments is always questionable in pesticide chemistry, and the present paper describes the results of a field trial at East Malling, Kent, designed to correlate the previous work with the behaviour under natural conditions.

EXPERIMENTAL

Apple trees provide a convenient model system on which to conduct spraying trials and have previously been used by workers in this laboratory for studying organochlorine pesticides[3]. The organophosphorus compounds examined in this field trial were selected to cover a wide range of hydrolyzability and included two pesticides, phorate and disulfoton, which had been previously examined in irradiation studies[2]. The levels and mode of application were different to those used in normal agricultural practice, *e.g.* phorate and disulfoton are usually applied as granular formulations and not as liquid formulations as used in the spray trial, but these changes were necessitated by the comparative nature of the experiment.

* Permission to publish has been given by the Government Chemist.

The "phosphorus detector" used in the gas chromatographic studies is able to tolerate large quantities of co-extracted materials and hence no clean-up of the leaf extracts was required; to prevent column contamination, however, a glass injection liner was used and this required daily cleaning.

Apple trees were sprayed with pesticides at the concentrations shown in Table I.

TABLE I

THE CONCENTRATIONS OF THE PESTICIDE SPRAYS

Pesticide	*Concentration (%, w/v)*
Demeton-S-methyl	0.2
Dimethoate	0.4
Disulfoton	0.6
Malathion	0.4
Mecarbam	0.4
Parathion	0.2
Phorate	0.6

Random samples of ten leaves were picked from the trees before spraying and at daily intervals thereafter. The leaves were stored in glass containers in chloroform and were usually extracted on the day after picking. The extraction procedure consisted of macerating each sample for 5 min with 30 g anhydrous, granular sodium sulphate and 50 ml chloroform. The mixture was drawn through a funnel fitted with a coarse glass sinter, the residue washed with a further 50 ml chloroform, and the combined extracts dried by passage down a column containing 10 g anhydrous sodium sulphate. The solution was evaporated to low volume in a Danish-Kuderna evaporator, the last traces of chloroform removed by a gentle stream of air and the residue dissolved in acetone. The extracts were stored in a refrigerator until all the associated extracts were available and the pesticide content then determined by gas chromatography. The gas chromatographic conditions have been previously described[4].

RESULTS

The initial pesticide levels on the apple leaves are shown in Table II and the decay patterns in Fig. 1.

TABLE II

THE INITIAL PESTICIDE LEVELS FOUND ON THE APPLE LEAVES

Pesticide	*Concentration (μg/leaf)*
Demeton-S-methyl	350
Dimethoate	800
Disulfoton	4,000
Malathion	700
Mecarbam	1,400
Parathion	350
Phorate	1,300

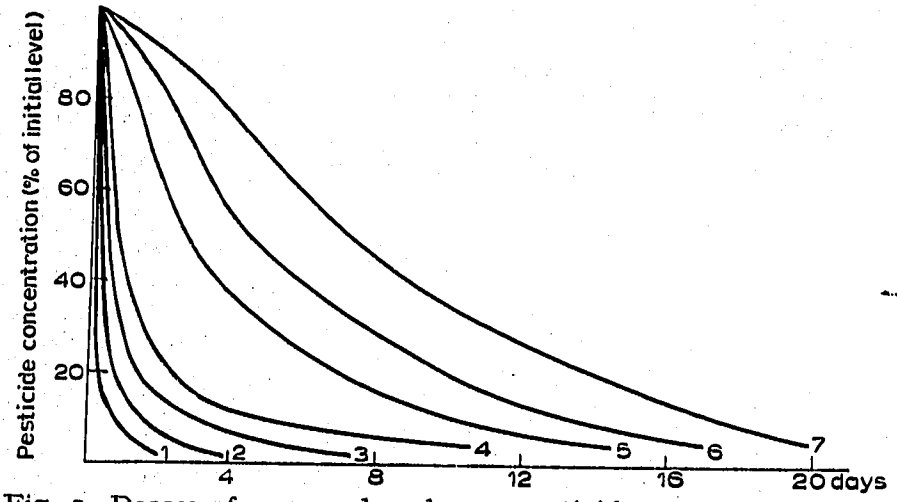

Fig. 1. Decay of organophosphorus pesticides on apple leaves. 1 = Phorate; 2 = demeton-S-methyl; 3 = disulfoton; 4 = parathion; 5 = malathion; 6 = dimethoate; 7 = mecarbam.

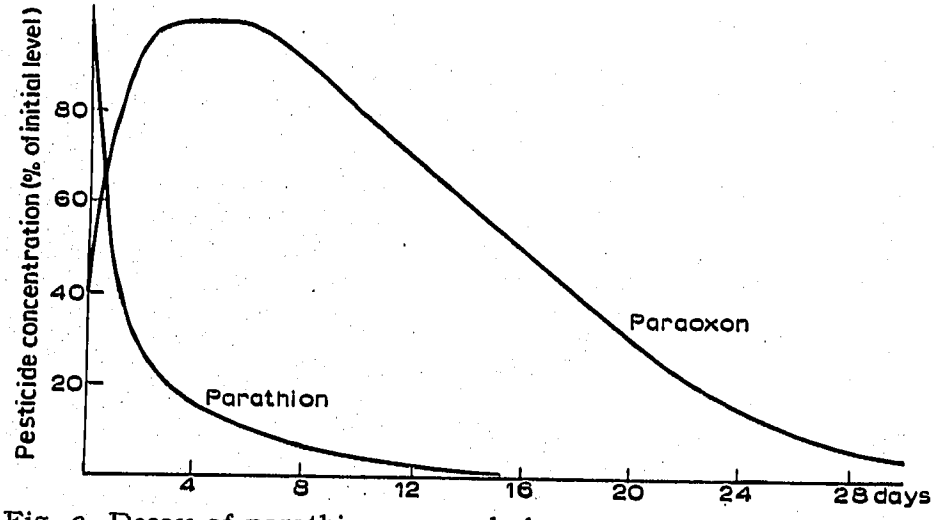

Fig. 2. Decay of parathion on apple leaves.

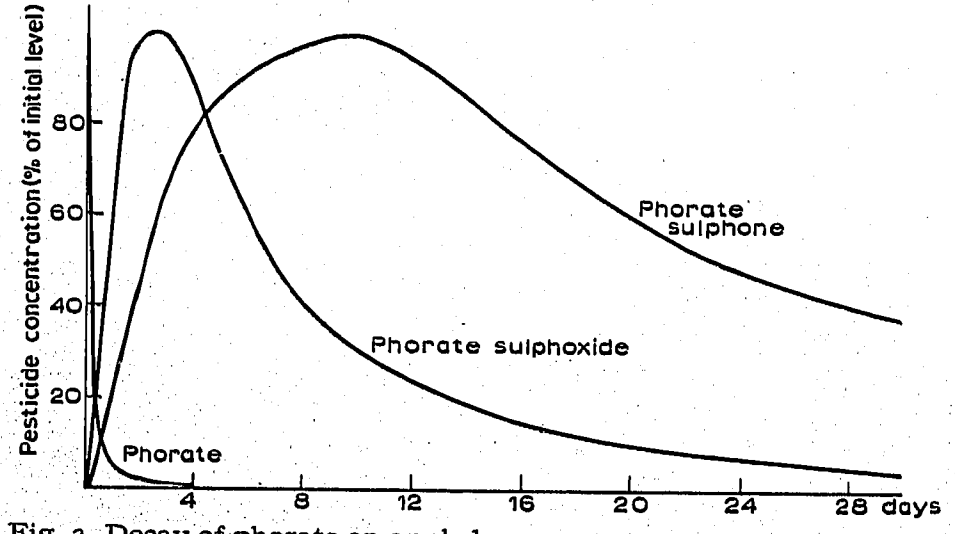

Fig. 3. Decay of phorate on apple leaves.

The pesticides demeton-S-methyl, dimethoate, malathion and mecarbam decayed without the formation of products detectable by gas chromatography. However, parathion, phorate and disulfoton formed products corresponding to their oxidation products in their gas chromatographic characteristics[4]. The decay pattern of parathion is shown in Fig. 2. Paraoxon was initially present at a level corresponding to 2 % of the parathion; after 15 days' exposure the levels were approximately equal and thereafter paraoxon predominated. In the case of phorate and disulfoton no pure standards of the oxidation products were available but the chromatogram indicated that the oxidation products were in excess of the parent compounds within two to four days. The decay curves are shown in Figs. 3 and 4.

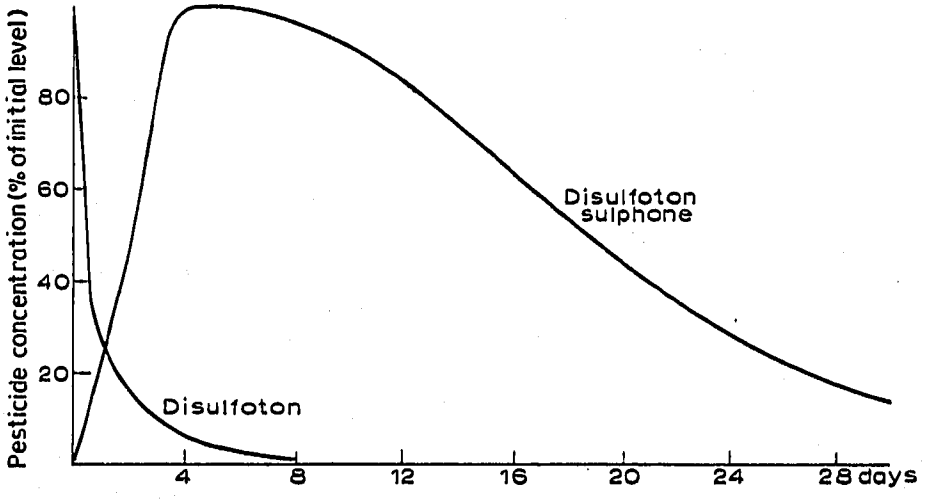

Fig. 4. Decay of disulfoton on apple leaves.

DISCUSSION

A logarithmic plot of the decay curves indicates that with the exception of mecarbam the decay follows close to first order kinetics. The half-lives are shown in Table III.

It is apparent that there is no direct correlation between the hydrolysis rates previously determined and the rate of decay on sprayed leaves. The decay curves of

TABLE III

COMPARATIVE RATES OF HYDROLYSIS OF THE PESTICIDES (HALF-LIVES)

Pesticide	*Half-life for hydrolysis*[1] *(hours) (laboratory exp.)*	*Half-life on field trial (days)*
Phorate	1.75	0.2
Demeton-S-methyl	7.6	0.5
Disulfoton	32.0	0.8
Parathion	43.0	1.0
Malathion	7.8	3.0
Dimethoate	12.0	4.3
Mecarbam	5.9	7.6

phorate and disulfoton (Figs. 3 and 4) show a marked similarity to those obtained during the ultra-violet irradiation studies[2] although in the case of disulfoton no sulphoxide was detected on the field trial samples. Parathion failed to produce paraoxon when irradiated under ultra-violet light in an analogous manner to that used previously[2]; dilute parathion standards in acetone (*ca.* 10 μg/ml), however, when allowed to stand in stoppered glass vessels in the laboratory for several weeks, produce appreciable quantities of paraoxon (*ca.* 50 % conversion). (We have observed similar behaviour with other dilute pesticide standards and it is now the practice in this laboratory to store a concentrated standard solution, *ca.* 1000 μg/ml, in the refrigerator and prepare sub-standards from this as required.) The absence of detectable oxidation products for four of the sprayed pesticides may be due to the inability of these materials to be chromatographed under the conditions used, *e.g.* demeton-S-methyl sulphoxide, or alternatively, being unable to resolve the oxidation products from the parent compound, as is the case with dimethoate and malathion on the column used.

The results indicate that the decay of pesticides on leaves is primarily controlled by a rate-determining irradiation process, apparently catalysing oxidation, and that hydrolysis acts in a secondary manner. Parent pesticides with an oxidizable side chain decay more rapidly than those without such groups but give rise to oxidation products which are considerably more stable and may also be more toxic.

CONCLUSIONS

Gas chromatography with the "phosphorus detector" provides a convenient method for following the decay of pesticides under field conditions. The decay rates vary with the pesticide and apparently are influenced more by the effects of light than by hydrolysis.

REFERENCES

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