Conversion of some Organo-Phosphorus Insecticides on Adsorbing Surfaces as Affected by Formulation

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One of the main functions of formulation is the optimization of physical properties of the active substance after application (URWYLER and EICHENBERGER, 1972; SOMERS, 1967; HARTLEY, 1966). It is well known that formulants strongly affect the physical properties of organo-phosphorus pesticides. It is also well known that adsorptive processes affect the chemical behavior and persistance of organo-phosphorus compounds (e.g. YIP and TSOU, 1971) and that these adsorption processes occur in soil with the adsorbents being clay minerals, organic materials and sesquioxides. However, the presence of various formulants might affect the adsorption processes, the formulants functioning as both adsorbates and adsorbents. Even on plant surfaces with the humidity and other conditions prevalent, the interaction between the active substance and the formulants will affect the chemical behavior, and specifically, the persistance of the pesticides.

This work was designed to investigate the effect of the manufacturers' formulations upon the behavior of Pirimiphos-ethyl and methyl and Menazon in the presence of natural adsorbents.

Materials and Methods

Sixteen ppm active ingredient solutions of Pirimiphos-ethyl (2-Diethylamino-6-methylpyrimidin-4-yl diethyl phosphorothionate); Pirimiphos-methyl (2-Diethylamino-6-methylpyrimidin-4-yl dimethyl phosphorothionate); JF2765 (Pirimiphos-ethyl emulsifiable concentrate); JF2764 (Pirimiphos-methyl emulsifiable concentrate); Menazon (S-(4,6-diamino-1,3,5-triazin-2-yl methyl) dimethyl phosphorothiolothionate); and Saphizon D.P. (formulated Menazon) in 0.4% W.W. acetone in water were prepared. All the pure and formulated insecticides were produced by ICI - Plant Protection Ltd. The above solutions were shaken with Ca-bentonite, Ca-kaolinite and Ca-peat (pH 5.5) with the ratio of 100:1 solution:solid, for 72 hours. Samples of the suspensions thus formed were taken at 0.5, 2, 5, 24 and 72 hours. The suspensions were centrifuged at 5000 rpm

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for 20 min and the supernatant was separated from the precipitate. After 5 hours and 72 hours, in the case of Pirimiphos-ethyl, Pirimiphos-methyl and their formulations, the precipitate was dried at room temperature overnight, and then extracted with hexane. UV spectra and GLC were taken from both the supernatant and the hexane extracts. The UV spectra were run on the Unicam SP 800 in the range of 190-450 mμ. The GLC was run on the Packard Gas chromatograph with the F.I. detector. The conditions for the GLC are as follows: glass column 90 cm x 3 mm I.D. filled with: a) 10% DC 200 + 15% QF-1 on Gas Chrom Q 80-100 mesh, or b) 10% SE-30 on Gas Chrom Q 80-100 mesh. Inlet and column temperature 220°C; detector temperature 200°C. Carrier gas flow: 75 ml per minute. The hexane extracts and 3:1 benzene:hexane extracts of the supernatants of Pirimiphos-ethyl, Pirimiphos-methyl and their formulations were injected.

The appearance of new or shifted peaks in the UV spectrum were taken as indications of chemical changes, while the decline in the main peak of the pesticides after 0.5 h of shaking was taken to indicate adsorption (Fig. 1 a-f). At the low concentrations used for the UV determinations, Beer-Lambert's low as assumed to hold. The GLC data was used as an independent method to confirm the UV data. The hexane extracts indicate the recovery rate of the adsorbed species, while the supernatant GLC indicate the amount left in solution. New peaks on the GLC indicate decomposition products.

All experiments were done at 25°C. All spectra were run against a blank of the 0.4% acetone solution shaken with the appropriate adsorbent. With all adsorbents the fraction smaller than 60 mesh was used. In the case of Ca-peat the fraction which was also heavier than water and insoluble in the 0.4% acetone solution was used.

Results and Discussion

Both GLC and UV were used as tools for following the kinetics of both adsorption and decomposition of the active pesticides in contact with the various adsorbents.

Table 1 compares the adsorption rates of the pesticides with and without formulations on the various adsorbents. Two interesting facts stand out here. Firstly, the unusual relatively high adsorption of Pirimiphos-ethyl upon Ca-kaolinite. Secondly, it seems that the adsorption of all pesticides is only slightly influenced by the presence of the formulants.

TABLE 1

Adsorption of Pirimiphos, Pirimiphos-methyl and Menazon with and without formulants from aqueous solutions*

(in percent)

Insecticide :	Pirimiphos-methyl		Pirimiphos-ethyl		Menazon	
Adsorbent	pure	with formulant	pure	with formulant	pure	saphizon
Ca-bentonite	94	95	92	100	16	18
Ca-kaolinite	30	27	75	80	5	5
Ca-peat	100	100	100	100	15	17

* 16 ppm pesticide solution-adsorbent ratio 100:1

On the other hand, the relative recovery rates of Pirimiphos-ethyl, Pirimiphos-methyl and their formulants by hexane extraction from the adsorbents, show a much more pronounced difference between formulated and non-formulated pesticides. For the same extraction technique, the recovery of formulated Pirimiphos-methyl and Pirimiphos-ethyl is between 40-50% greater than that of the pure materials. This phenomenon may have further effects on the transport processes and pesticide potency in soil.

Evidence of the effect of formulation on the conversion of Pirimiphos-ethyl and methyl is shown in Tables 2 and 3. The appearance rate of metabolites in the supernatant was determined. The numbers given in the tables represent the ratio between the intensity of the absorption due to the metabolits and the maximum absorption of the standard pure pesticide. The actual numbers are one hundred times this ratio. As can be seen in Fig. 1, the values in Tables 2 and 3 are useful only for comparison purposes and are of limited absolute accuracy.

TABLE 2

Relative appearance rate of Pirimiphos-methyl metabolites in the aqueous solutions

Adsorbent :	Ca-bentonite		Ca-kaolinite		Ca-peat	
Time (h)	pure	with formulant	pure	with formulant	pure	with formulant
0.5	nd	nd	nd	nd	nd	nd
2.0	2.5	1.5	nd	nd	nd	nd
24.0	4.0	2.0	nd	nd	nd	nd
72.0	4.0	2.0	nd	nd	nd	nd

nd = non detectable

TABLE 3

Relative appearance rate of Pirimiphos-ethyl metabolites in the aqueous solutions

Adsorbent :	Ca-bentonite		Ca-kaolinite		Ca-peat	
Time (h)	pure	with formulant	pure	with formulant	pure	with formulant
0.5	nd	nd	nd	nd	nd	nd
2.0	4.0	nd	nd	nd	nd	nd
24.0	10.0	7.0	nd	nd	5.0	3.5
72.0	12.0	7.5	4.0	nd	15.0	4.5

nd = non detectable

Figure 1 a-f gives the UV spectra of the formulated and non-formulated pesticides as well as the spectra of the supernatant after shaking the pesticides solutions in the 0.4% acetone aqueous solution with Ca-bentonite after 0.5 and 72 hours. Note the absence of new peaks or shoulders in the Menazon

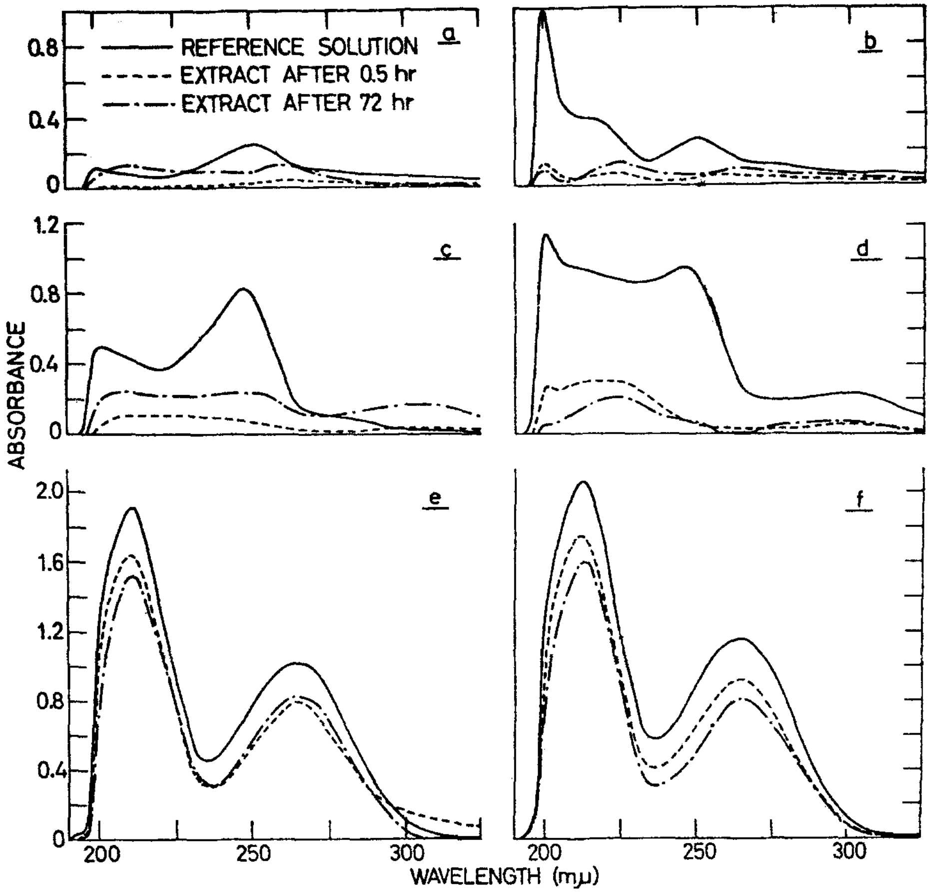

Fig. 1: UV spectra of standard solutions and extracts from Ca-bentonite suspensions in aqueous solution of:

a) pirimiphos-ethyl; b) formulated pirimiphos-ethyl; c) pirimiphos-methyl; d) formulated pirimiphos-methyl; e) menazon; and f) formulated menazon.

and Saphizon spectra. Menazon metabolites were thus undetected up to 72 hours. That some chemical change occurred in Menazon but not in Saphizon is suggested by the change in the ratio between the two peaks in Figure le after 72 hours. In all cases checked, formulation retarded the rate of decomposition at the surfaces, unless metabolites produced in the presence of the formulants were adsorbed preferentially to metabolites produced in their absence.

Thus, even this preliminary data using arbitrary formulations, indicate the potential stored in the use of formulants for the purpose of affecting the chemical and biological behavior of pesticides after application. At present, the possibility that the effect of the formulations on the pesticides in contact with the adsorbents is not direct, but is through the effect of the formulants on the adsorbents (dispersing or flocculating) cannot be excluded. At any rate, it is possible to state that the formulations affect the persistance and phase distribution of the pesticides. It stands to reason that other formulants specifically selected to affect the chemical behavior of pesticides in soil may have an even more pronounced effect.

References

1. HARTLEY, G.S. "The Formulation of Pesticides," S.C.I. Monograph 21, 122, (1966).

2. TORGESON, D.C. Fungicides, Vol. 1, 153, (1967).

3. URWYLER, H. and EICHENBERGER, J.E. Proc. 2nd Internl. IUPAC Cong. of Pesticide Chemistry, Vol. V, 425, (1972).

4. YIP, K.F. and TSOU, K.C. J. Am. Chem. Soc. 93, 3272, (1971).

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