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Study on the Stability of Leptophos in Water Under Laboratory Conditions

M. R. Riskallah, M. M. El-Sayed, and S. A. Hindi

Central Agricultural Pesticides Labroatory, Institute of Plant Protection, Agricultural Research Center, Dokki, Giza, A.R. Egypt

Leptophos, O-(4- bromo - 2,5-dichlorophenyl) O-methyl phenylphosphonothioate, is a phosphonate insecticide whose residues on sprayed plants disappear less rapidly than do many organophosphorus insecticids (LEUCK et al. 1970, AHARONSON and BEN-AZIZ 1974). Indications that this compound have neurotoxic properties were described by ABOU-DONIA and PREISSIG(1976). Although leptophos effectively controlled cotton pests in Egypt (ZEID et al. 1973), there were cases of poisoning of several hundreds of water buffaloes where it was used in the Nile Delta in 1971 (ANONYMOUS 1971). In some cases paralysis of hind limps were observed long after the spraying season was over (SHEA 1974). The fate of leptophos in local environment was, therefore, undertaken. Previous study in our laboratory indicated that leptophos is a rather stable insecticide, since after exposure to ultraviolet light for 24 hours or to direct sunlight for 65 days, relatively large quantity of the original chemical (ca. 37% - 47%) remained unchanged (RISKALLAH 1975). The purpose of the present work is to investigate the stability of leptophos in several samples of water collected from different sources in Giza province during the Summer 1977.

MATERIALS AND METHODS

Samples preparation. Samples from six water sources were collected from Giza province during July 1977. Before starting the experiment, a part from each original sample was used to determine the values of total hardness (Ca. + Mg) by the method of SCHWARZENBACH and BIEDERMAN (1948), pH, and total solids. PH values were also determined at the end of the experiment. (Table 1). 500 ml from each sample were placed in 1 litre dark glass container, and proper aliquot of leptophos (30% Emulsifiable concentrate, EC)were added to each sample to give a concentration of 1.18 µg active ingredient per ml. The containers were tightly closed and the experiment were performed at room temperature (25 + 2°C).

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TABLE 1

Some chemical and physical properties of different water samples collected from various sources in Giza province.

Source of water	Total hardness (p.p.m)[a]	% Total solids	pH[b]	
			A	B
1- Distilled water	0.0	0.0	6.6	7.1
2- Tap water	156	0.0172	7.2	7.3
3- Artisian well	264	0.0172	8.0	7.9
4- Mansoria-irrigating canal.	180	0.0220	8.0	7.9
5- Marioteia-drainage canal.	348	0.0436	8.0	7.5
6- River Nile	160	0.0226	8.5	8.2

a. calculated as sodium carbonate.

b. A and B were the values of pH at the beginning and at the end of the experiment, respectively.

Extraction procedure: Extraction was carried out according to the method of BRAUN (1974) with slight modifications. At the selected time intervals (Table 2), two replicates (25 ml each) representing each sample were pipetted into 250 ml separatory funnel followed by 20 ml benzene, and shaken vigorously for 1 minute. 70 ml of aqueous carbonate solution (1%) were added and shaken again for 1 minute. Benzene extracts were washed by shaking with 10 ml distilled water for 30 seconds, allowed to pass through cotton pad with anhydrous sodium sulphate, and collected in 100 ml boiling flask. The separatory funnel was rinsed with 5 ml benzene and rinsings were combined with benzene extracts and concentrated to 5-10 ml using rotary vacuum evaporator at 40°C.

Gas-chromatography: Leptophos in benzene extracts was determined using a Pye-Unicam (104) gas chromagraph equipped with flame-photometric detector sensitive to phosphorus (526 nm filter) under the following parameters : column—glass, 6 feet x 4 mm.id. packed with 4% SE-30 + 6% OV-210 on 80-100 mesh

chromosorb Q, preconditioned 72 hours at 250°C; gas flows (ml/minute)—nitrogen 100, oxygen 20, air 90, and hydrogen 100; temperatures— column 250°C, detector 187°C.

Recovery studies: For recovery estimation, a known amount of pure leptophos (30 ug) was added to 25 ml distilled water into separatory funnel. The fortified sample was then carried through the analytical procedure as mentioned before. The percent recovery was calculated from two replicates and found to be 95.27%.

RESULTS AND DISCUSSION

The present data indicated that leptophos suffered degradation when held in different water samples at room temperature. Table (2) represents the amounts of leptophos recovered from different water samples after several periods of storage. Table (3) represents the retention times and the appearance of different degradation products which appeared as G.C. peaks under the present conditions of analysis. It is clear that leptophos was degraded to 7 unidentified degradation products which contain the phosphorus atom in their chemical structure, since they were analysed by a phosphorus sensitive detector.

Insecticide degradation in either soils or waters were greatly affected by the presence of microorganisms, clay, colloidal particles, and organic matter. (EDWARDS 1973, and BROWN 1978). Accordingly to discuss the present data it is more convenient to divide the water samples under investigation into two groups (Tables 2, and 3). Group (I) include distilled water, tap water, and artisian water; which could be considered almost free from clay, organic matter, and microorganisms. Group (II) represents the River Nile, irrigating canal, and drainage canal waters, which expected to contain some of the above mentioned constituents.

An interesting feature of the present data is that the rate of leptophos breakdown was higher in water samples of group (I) than in water samples of group (II). After 16 weeks, 2.8-39% of the original amount of leptophos were still remaining unchanged in distilled, tap, and artisian waters, while higher percentages (43% - 100%) were detected in case of River Nile, irrigating, and drainage waters (Table 2). These results could be explained according to the observations of ROBERTS (1963), KARINEN et al. (1967), POTER and BEARED (1968), and EDWARDS (1973) who reported

TABLE 2

The amount of remained leptophos, expressed as percent of initial[a] detected in different types of water after storage in closed glass containers for several periods at room temperature following leptophos treatment.

Storage period	Type of Water					
	Distilled water	Tap water	Artisian water	Irrigating water	Drainage water	River Nile water
3 Days	85.5	48.6	49.7	86.3	80.2	-
1 Week	53.2	33.9	23.2	82.3	78.8	68.8
2 Weeks	-	33.6	22.6	81.0	67.2	66.0
4 Weeks	52.2	15.2	20.1	69.6	76.2	54.9
8 Weeks	39.5	6.0	19.0	65.9	100.0	54.7
16 Weeks	39.0	2.8	12.4	62.4	105.3	43.3

a . Initial concentration (zero time samples) was 1.18 ug/ml.

TABLE 3

Leptophos and its degradation products detection by G.C.[a] in different types of water after storage in closed glass containers for several periods at room temperature.

Storage period	Compounds detected in different types of water					
	Group (I)			Group (II)		
	Distilled water	Tap water	Artisian water	Irrigating water	Drainage water	River Nile water
3 Days	L	G,L	L	L	L	L
1 Week	L	G,L	G,L	L	L	L
2 Weeks	B,C,D,G,L	G,L	G,L	L	G,L	G,L
4 Weeks	A,C,F,G,L	C,G,L	C,G,L	C,G,L	C,G,L	C,G,L
8 Weeks	C,G,L	E,F,G,L	L	C,G,L	L	L
16 Weeks	G,L	E,F,G,L	G,L	G,L	G,L	L

a Retention times relative to ethyl parathion were 2,76, 2,64, 1,28, 0,72 0,56, 0.36, 0,28, and 0,20 for leptophos (L) and the degradation products A,B,C,D,E,F, and G respectively.

that the degradation rate of several pesticides was markedly reduced in the presence of clay, colloidal particles, and organic matter, which were expected to be present, even in low quantities, in waters of group (II) and not in waters of group (I). Also, the present results could be attributed to the relatively higher values of total hardness (calcium + magnisium) of waters of group (II) than that of waters of group (I), as magnesium was reported to decrease the rate of insecticides degradation (SWANSON et al. 1954, and EDWARDS 1973).

A comparison between water samples of group (I) revealed that leptophos declined at a higher rate in tap and artisian waters than in distilled water. This result could be expected in case of artisian water owing to its relatively alkaline pH value (Table 1) and according to the fact that most organophosphorus compounds decline rapidly under alkaline conditions (KONARD and CHESTER 1969, EDWARDS 1973, and BROWN 1978). In case of tap water the observed high rate of leptophos degradation might be related to the presence of some minerals such as iron, copper, or lead which were reported to be important in influencing the breakdown of insecticides (EDWARDS 1973).

In case of water samples of group (II), the results of Table (2) indicate that River Nile water influenced leptophos degradation at a slightly higher rate than did the other two water samples. This finding would be easily explained on the basis of the comparatively higher pH value of River Nile water, even at the end of the experiment period (Table 1).

It was of considerable interest to note that, in case of drainage water, leptophos declined to 67.2% of its initial concentration after 2 weeks, but a marked increase in leptophos amount took place after that to reach its initial amount again at the end of the investigation. To explain this unexpected data, it should be mentioned that there is a noticeable difference between drainage water and the other waters under study, where the values of total solids, and total hardness were relatively higher in drainage water (Table 1). Also, it is generally known that drainage water is often calm while the other waters are running off, a difference which may rise the probability that drainage water contain some microorganisms which may be absent in the other waters. The presence of certain microorganisms in drainage water could be indicated by the appearance of a considerable degree of turbidity into drainage water container and by the drop in pH

value (Table 1) which probably reflect the anerobic conditions prevailing the end of the experiment. In view of these differences between drainage water and the other waters, there is a probability that leptophos may be degraded in drainage water in a different way from that in other waters to give certain products which has the same retention time of leptophos itself, resulting in increasing the actual amount of leptophos present in the sample. However, we do not have enough evidence to assess this assumption and further investigations are required in order to clearly understand the fate of leptophos in drainage water.

In conclusion, leptophos proved to be a rather stable compound, as after 4 months a considerable amount of this compound was still remaining unchanged in different water samples. The high stability of leptophos in water was more pronounced in River Nile, irrigating, and drainage waters where 43% to 100% of its initial amount were detected unchanged at the end of the experimental period. These data are in harmony with the relatively high stability of leptophos in soil (HARRIS and MILES 1975), on sprayed plants (LEUCK et al. 1970, and AHARONSON and BEN-AZIZ 1974), and when exposed to ultraviolet or direct sunlight (RISKALLAH, 1975). All of these observations came to the same conclusion that leptophos could be considered as one of the most persistent organophosphorus compounds in the environment.

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