

Persistence of Dichlobenil in a Farm Pond

A farm pond in New York State was treated with dichlobenil (2,6-dichlorobenzonitrile) at the rate of 10 lb of active ingredient per surface acre and residues of the herbicide were determined in both the water and hydrosol. Maximum concentrations of dichlobenil measured in the water and hydrosol were 1.4 and 8 ppm, respectively. These

concentrations were found in samples taken 7 days after treatment. After 7 weeks, 85 and 78% of the maximum detected levels of the herbicide in the water and hydrosol, respectively, had disappeared. The concentration of dichlobenil had decreased to 0.002 ppm in the water and 0.13 ppm in the hydrosol, 140 days after treatment.

The herbicide dichlobenil (2,6-dichlorobenzonitrile) has been found to be effective against a variety of aquatic weeds (Frank *et al.*, 1963; Walker, 1964). If water treated with an herbicide is to be consumed by humans or livestock or used for irrigation, its use must be restricted until the residues decrease to safe levels. Small amounts of herbicide residues may also exert detrimental effects on the aquatic fauna and flora. Therefore, it becomes necessary to study the persistence of herbicides in the aquatic environment.

Van Valin (1966) and Frank and Comes (1967) studied the persistence of dichlobenil in farm ponds in Denver, Colo., following an application of the herbicide as a granular formulation at the rate of 10 lb of active ingredient per surface acre, or about 0.6 ppm. They observed that dichlobenil persisted in both the water and soil for periods exceeding 160 days. Walsh *et al.* (1971) found that in ponds near Pensacola, Fla., treated with 1 ppm of dichlobenil as a wettable powder, the concentrations of the herbicide in water and hydrosol were 0.001 and 0.004 ppm, respectively, 64 days after treatment. Ogg (1972) observed that in a pond near Corvallis, Ore., treated with dichlobenil as a wettable powder and granular formulations at 10 lb of active ingredient per surface acre, the herbicide could be detected in the water and hydrosol up to 126 days after treatment. The herbicide was found to disappear rapidly during the first 5 weeks following treatment. The concentration of dichlobenil was higher in the hydrosol than in the water in all these studies discussed above.

The above studies deal with the persistence of dichlobenil in ponds located in the northwestern, west central, and southeastern regions of the United States. However, no information is available on the persistence of the herbicide in ponds under the climatic conditions prevailing in the northeastern United States. Since weather and climate influence the persistence of an herbicide through their effect on volatilization and biological and nonbiological degradation, the herbicide residue levels resulting from herbicide application may vary under different climatic conditions. The present investigation was undertaken to obtain information on the persistence of dichlobenil in a pond in New York State.

MATERIALS AND METHODS

Treatment of Pond. A farm pond located about 6 miles west of Syracuse, N. Y., was selected as the test site. The pond had a surface area of 0.13 acre and an average depth of 5 ft. It was spring-fed and had no outlet. The pH of the pond water at the time of treatment was 8.5 and the water temperature near the surface of the pond ranged from about 18° on the day of treatment to about 30° 3 months after treatment when most of the dichlobenil had disappeared from the water. The physical and chemical properties of the hydrosol were: pH 7.7; cation exchange capacity, 2 mequiv/100 g; organic matter, 4.0%; sand, 24%; silt, 57%; clay, 19%. The soil texture was silt loam.

The pond was treated in May 1971 with a 10% granular formulation of dichlobenil at the rate of 10 lb of active in-

gradient per surface acre. The granules were spread uniformly over the surface of the pond. Water and hydrosol samples were taken from the pond 1 day after treatment and periodically thereafter up to about 4 months after application. On each of the sampling dates, four 1-l. water samples were taken at 2- to 3-ft depths from different areas of the pond. Hydrosol samples were likewise taken from four different areas of the pond. The hydrosol samples were collected from the top layer to a depth of approximately 1 in. with a small clam-type dredge. Both the water and the hydrosol samples were composited separately, thoroughly mixed, and stored frozen in glass bottles until ready for analysis. From each composite sample, duplicate samples were withdrawn for analysis. Pretreatment samples of soil and water were obtained for herbicide recovery and background studies.

Analysis of Water and Hydrosol. The methods described by Meulemans and Upton (1966) and Van Valin (1966) were used with slight modifications to determine the residues of dichlobenil in the water and hydrosol samples. The water samples were extracted by vigorously shaking 500-ml aliquots in a 1000-ml separatory funnel with three successive portions of 50, 25, and 25 ml of pesticide-grade benzene. The volume of the combined extracts was measured and the amount of dichlobenil was determined by electron capture gas-liquid chromatography. Excess water was removed from the hydrosol samples by suction filtration prior to analysis. The wet soil, weighing 100 g, was extracted three times with a total of about 200 ml of pesticide-grade benzene by shaking the mixture vigorously in a round-bottomed flask. After each extraction, the benzene extract was decanted. The three extracts were combined and, after allowing the solid material to settle, the pooled extract was filtered by suction filtration. The benzene extracts from water and soil samples were dried over anhydrous sodium sulfate. The total volume of the filtrate was measured and the solution was analyzed directly by gas-liquid chromatography. When the extract contained less than 0.03 ppm of the herbicide, it was concentrated in a Kuderna-Danish evaporator prior to analysis. A Micro-Tek Model 220 gas chromatograph equipped with a ⁶³Ni electron capture detector was used for analysis. The chromatographic column, an 800 cm × 4 mm (i.d.) borosilicate glass U-tube, was packed with 5% DC-200 on Gas Chromosorb P (100-120 mesh). Operating temperatures for the various components were as follows: inlet, 225°; oven, 183°; detector, 275°. The carrier gas was nitrogen with a flow rate of 118 ml/min. The amount of dichlobenil in the water and hydrosol extracts was determined from peak height measurements which were compared with those of standard dichlobenil solutions.

To determine the per cent recovery of dichlobenil from the water and hydrosol, known quantities of dichlobenil, ranging from 0.1 to 5.0 ppm, were added to the soil and water samples. The soil was allowed to equilibrate with the herbicide for 2-3 hr prior to analysis. The fortified samples were then analyzed for dichlobenil as described above. The recovery factor was used to correct the levels found in the hydrosol.

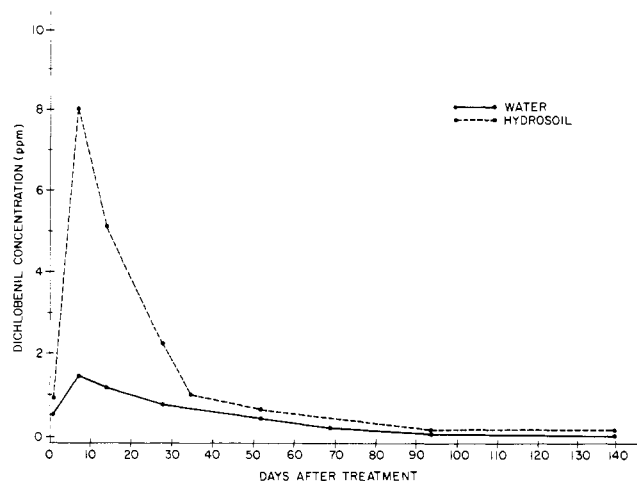


Figure 1. Dichlobenil residues in water and the top 1 in. of hydrosoil of a treated farm pond, with time.

RESULTS AND DISCUSSION

The retention time for authentic dichlobenil was 1.02 min and the lower limit of detection for the herbicide was 0.15 ng. The recovery of dichlobenil from fortified samples of water and hydrosoil averaged 98 and 90%, respectively.

Figure 1 shows the concentration of dichlobenil in the pond water and top 1-in. layer of hydrosoil at various times after treatment. The values appearing in this figure are the average of duplicate determinations. Among the water samples taken, the highest concentration of dichlobenil (1.41 ppm) was detected 7 days after treatment. Thereafter, the concentration of dichlobenil declined gradually, reaching 50% of the maximum detected level 28 days after treatment. Only traces of the herbicide (0.002 ppm) were detected in the water 140 days after treatment. As in the water, the highest concentration of dichlobenil in the hydrosoil (8 ppm) was found in the sample taken 7 days after treatment. Thereafter, a rapid decrease in the concentration of dichlobenil occurred in the hydrosoil and only 22% of the maximum detected level remained 35 days after treatment. This initial, rapid rate of disappearance was followed by a more gradual decrease which paralleled the rate of loss of dichlobenil in the water. The concentration of the herbicide in the hydrosoil had decreased to 0.13 ppm 140 days after treatment when the last sample was taken.

Thus, both in water and hydrosoil, we observed a pattern of increase of the herbicide residues followed by a decrease. The fact that a higher concentration of dichlobenil was detected on the seventh day than on the first day after treatment indicates that the herbicide was not re-

leased into the water and hydrosoil immediately after application. Presumably, the lag in reaching the maximum concentration was caused by the slow dissolution of the granular formulation. The disappearance of dichlobenil from the water may be attributed to volatilization (Massini, 1961), microbial degradation (Verloop and Nimmo, 1970), and photodecomposition (Plimmer and Hummer, 1968), whereas microbial degradation, absorption of the herbicide by aquatic vegetation, and possibly leaching to lower depths may have been the contributing factors in the disappearance of dichlobenil from the hydrosoil. The maximum concentration of the herbicide measured in the hydrosoil exceeded that in the water through the first 4 weeks. This may have been due to the tendency of dichlobenil to adsorb to soil (Massini, 1961) and to the low solubility of the herbicide in water.

The results show that small amounts of dichlobenil remained in water and hydrosoil for an extended period under the experimental conditions. The degree of dissipation of the herbicide in our experiment is comparable to that reported for ponds in Oregon and Colorado (Van Valin, 1966; Frank and Comes, 1967; Cope *et al.*, 1969; Ogg, 1972) but is slower than that reported for ponds in Florida (Walsh *et al.*, 1971).

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An Analysis of the Phytosterols of Two Varieties of *Cannabis*

The quantitative determination of the 3- β -hydroxysterols in American-grown (MS-13) and Thailand-grown *Cannabis* has been accomplished. The Thailand sample showed no free sterols although it contained the highest total

sterol content. No campesterol was found as the glycoside in the MS-13 and Thailand sample while the Thailand sample contained no stigmasterol as the glycoside.

The 3- β -hydroxysterols campesterol, stigmasterol, and β -sitosterol have recently been identified in extracts of *Cannabis* (Doorenbos *et al.*, 1971; Fenselau and Hermann, 1972). These phytosterols have also been found in tobacco (Stedman, 1968; Keller *et al.*, 1969) and have been implicated as precursors of carcinogenic hydrocarbons in its

smoke (Wynder *et al.*, 1959). As we have found the phytosterols to constitute approximately 1% of the neutral compounds in the smoke condensate of *Cannabis*, it was of interest to determine their levels in the plant material.

Quantitative analyses of sterol content were performed on *Cannabis* grown at the University of Mississippi (MS-