lyze further to biodegradable materials such as malonic acid (Krieble and Noll, 1939; Malaney and Gerhold, 1969). Chemicals or microorganisms in soil can decompose DBNPA. Microbial degradation of DBNPA has been demonstrated by the use of tracer techniques. For example, DBNPA-2-^{14}C yielded 40% $^{14}CO_2$ after 2 weeks in the presence of unaerated waste treatment sludge (Wolf, 1971). Thus, hydrolytic, photolytic, chemical, and microbial decomposition of DBNPA and its degradates suggests that these compounds will not persist in the environment.

The question of bioconcentration of DBNPA in the environment must be considered along with the persistence of the compound. Metabolic studies on rats (Rose, 1971) with DBNPA-2-^{14}C indicate that DBNPA is cleared rapidly from the body. This fact and the low lipid affinity of DBNPA ($P_{octanol/H2O}$ = 6.1) suggest a low potential for bioconcentration (Wolf, 1971).

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LITERATURE CITED

American Public Health Association, "Standard Methods for the Examination of Water and Waste Water," 13th ed., 1971, No. 218B, p 477.
Dinglinger, A., Schroer, E., *Z. Phys. Chem. Abt. A* **179,** 401 (1937).
Dinglinger, A., Schroer, E., *Z. Phys. Chem. Abt. A* **181,** 375 (1938).
Freeman, F., *Chem. Rev.* **69,** 591 (1969).
Hammett, L. P., "Physical Organic Chemistry," 1st ed., McGraw-Hill, New York, N. Y., 1940, pp 353-354.
Hesse, B. C., *J. Amer. Chem. Soc.* **18,** 725 (1896).
Jensen, H. L., *Acta Agr. Scand.* **10,** 83 (1960).
Kleinert, S. J., Degurse, P. E., *Wis. Dep. Nat. Resour. Res. Rep.* **73** (1971) (in Matsumura, F., Gotah, Y., Boush, C. M., *Science* **173,** 49 (1971)).
Kolthoff, I. M., Sandell, E. B., "Textbook of Quantitative Inorganic Analysis," 3rd ed., MacMillan, New York, N. Y., 1952, pp 372-375.
Krieble, O. K., Noll, C. I., *J. Amer. Chem. Soc.* **61,** 560 (1939).
Larsson, E., *Trans. Chalmers Univ. Technol., Gothenburg* **No. 51,** 3 (1946); *Chem. Abstr.* **41,** 3684b (1947).
Malaney, G. W., Gerhold, R. M., *J. Water Pollut. Contr. Fed.* **41** (Pt 2), R18 (1969).
Nolan, H. K., Hechenbleikner, I., to American Cyanamid Co., U. S. Patent 2,419,888 (April 29, 1947).
O'Connor, C., *Quart. Rev.* **24,** 553 (1970).
Parham, W. E., Schweizer, E. E., *J. Org. Chem.* **24,** 1733 (1959).
Rose, J. Q., The Dow Chemical Company, Midland, Michigan, private communication, 1971.
Stevens, C. L., Dittmer, H., Kovacs, J., *J. Amer. Chem. Soc.* **83,** 3394 (1963).
Wilt, J. W., *J. Org. Chem.* **21,** 920 (1956).
Wolf, P. A., The Dow Chemical Company, Midland, Michigan, private communication, 1971.
Wolf, P. A., Sterner, P. W., *Appl. Microbiol.* **24,** 581 (1972).

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Persistence of Endothall in Aquatic Environment as Determined by Gas-Liquid Chromatography

Harish C. Sikka* and Clifford P. Rice

A gas chromatographic method was used to determine the residues of endothall in both the water and hydrosoil of a farm pond and of laboratory aquaria. The bulk of endothall added to the aquaria remained in the water during the course of the experiment. Both in the pond and in the aquaria, the herbicide persisted in the hydrosoil for a longer period than in the water. In the pond treated with approximately 2 ppm of endothall, the herbicide could not be detected in the water and top 1 in. of the hydrosoil 36 and 44 days after treatment, respectively. In the aquaria treated with 2 and 4 ppm, endothall was reduced to nondetectable levels in the water within 7 days after treatment. It took 2 and 4 weeks for the herbicide in the hydrosoil to reach a level of less than 0.1 ppm in the aquaria treated with 2 and 4 ppm, respectively. The rate of endothall dissipation in the aquaria was similar at both application rates.

The herbicide endothall (7-oxabicyclo[2.2.1]heptane-2,3-dicarboxylic acid) has been found to be effective in controlling certain submersed aquatic weeds (Frank *et al.*, 1961; Walker, 1963). In cases where the treated water is to be consumed by humans and/or livestock or used for irrigation, it becomes imperative that we have information on the persistence of the herbicide in the aquatic environment. Hiltibran (1962) studied the persistence of endothall in pond water, both in aquaria and under field conditions. In the field, endothall applied at 0.3 to 10 ppm could not be detected after an average of 2.5 days and a maximum of 4 days. In aquaria, endothall at these rates was detectable for a much longer period. The rate of disappearance of endothall varied directly with the amount of organic material and organisms present in the water. In studies dealing with the disappearance of the di-*N,N'*-dimethylcocoamine salt of endothall, Walker (1963) found that detectable residues of the herbicide had disappeared within 8 days following application of 0.3 ppm and within 2 weeks for 0.6 ppm. However, 1 to 3 ppm of the herbicide took up to 25 days to disappear. Frank and Comes (1967) observed that in a pond treated with 1 ppm of the di-*N,N'*-dimethylcocoamine salt of endothall, the herbicide could not be detected 24 days after treatment. Yeo (1970) reported that in some ponds treated with the dipotassium salt of endothall, the initial concentrations of 0.3 to 1.4 ppm dissipated to less than 0.03 ppm in 8 to 20 days, while in others the average dissipation was about 71% during the same period. In growth pools treated with 0.5 to 4 ppm of endothall, about half the initial concentration had disappeared within 12 days.

In most of the above studies, endothall residues were determined using a flaxseed bioassay method first described by Hiltibran (1962). This method has the limitations inherent in a bioassay, namely it is indirect, and is more time consuming, less precise, and less quantitative than a chemical assay. Frank and Comes (1967) used a

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colorimetric method for detection of the amine salt of endothall. However, this method is specific only for this endothall formulation since it is based on the detection of the amine substituent of endothall and not of endothall. Presently very little information is available on the persistence of endothall in hydrosoil since the above investigators studied only the disappearance of endothall in water. In any study dealing with the persistence of an aquatic herbicide, it is important that the residue levels of the chemical also be determined in the hydrosoil since the soil particles form a reservoir which may supply herbicide to the water over a period of time.

The present investigation was undertaken to determine the persistence of endothall both in water and hydrosoil under field conditions and in aquaria. In these studies, the residues of endothall were determined using an analytical method which involves gas–liquid chromatography. This method is specific for the determination of endothall and is more sensitive than methods used previously.

MATERIALS AND METHODS

Treatment of Farm Pond and Aquaria. For the field studies, a farm pond located 4 miles west of Syracuse, N. Y., was selected as the test site. The pond had a surface area of about 0.1 acre and an average depth of 4 ft. The pond was spring-fed and had no outlet. Endothall was applied to the pond as the dipotassium salt of endothall (Aquathol K) at a rate of 2 ppm of endothall. Even distribution of endothall was obtained by spraying a water solution of the herbicide uniformly over the surface of the pond. Water and hydrosoil 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 2–3-ft depths from different areas of the pond. Hydrosoil samples were likewise taken from four different areas of the pond. The hydrosoil samples were collected from the top layer to a depth of approximately 1 in. with a small clam-type dredge. Pretreatment samples of soil and water were obtained for herbicide recovery and background studies.

For the laboratory studies, two 10-gal capacity aquaria, containing 7 gal of the pond water and 1½ in. layer of pond hydrosoil, were placed in a constant-temperature (25 ± 1°) room. After a 7-day equilibration period, the aquaria were treated with the dipotassium salt of endothall at rates of 2 and 4 ppm of endothall in the water. Samples of water (800 ml) and hydrosoil (200 g) were taken 4 hr and 1, 3, 7, 21, 28, and 35 days after treatment.

The water as well as the hydrosoil samples from both the pond and aquarium studies were composited, thoroughly mixed, and stored frozen until ready for analysis. From each composite sample, duplicate samples were withdrawn for analysis.

Pond Water and Hydrosoil Properties. The properties of the pond water at the time of treatment were: pH 8.7; alkalinity, 91.6 mg/l. (expressed as carbonate); and hardness, 68 mg/l. (calcium and magnesium ion expressed as calcium carbonate). The water temperature near the surface of the pond ranged from about 21° on the day of treatment to about 24° 4 weeks after treatment, when most of the endothall had disappeared from the water. The physical and chemical properties of the hydrosoil were: pH 7.8; cation exchange capacity, 5 mequiv/100 g; organic matter, 10.2%; sand, 24%; silt, 59%; and clay, 17%. The soil type was silt loam.

Analysis of Water. The method of analysis used to determine the residues of endothall in water and hydrosoil samples was essentially the same as that developed by the Agricultural Chemicals Division of Penwalt Corporation (Pennwalt Corporation, 1972). Slight modifications were made for operational convenience and efficiency. In this method, endothall in the sample is converted to endothall *N*-chloroethylimide by reaction with 2-chloroethylamine hydrochloride. The concentration of the imide derivative is determined using a gas–liquid chromatograph equipped with a nitrogen-specific detector.

Duplicate 200-ml samples of water were acidified to pH 1 with concentrated HCl and evaporated to about 50 ml on a hot plate. About 200 ml of glacial acetic acid was then added and the solution was concentrated in a hood to about 30 ml by heating it to a temperature of 118°. The solution was further concentrated to about 5 ml with the aid of a stream of air. The concentrated solution was transferred to a small beaker with 10 ml of acetic acid. To convert endothall to its *N*-chloroethylimide derivative, 100 mg each of 2-chloroethylamine hydrochloride and anhydrous sodium acetate was added and the solution was heated for 1 hr on a hot plate (with the surface temperature adjusted to 120°). The solution was then transferred with 50 ml of water to a separatory funnel and extracted with four 20-ml portions of chloroform. The pooled chloroform extract containing the chloroethylimide derivative was evaporated almost to dryness using low heat and a stream of air. The residue was immediately dissolved in 0.5 ml of methanol to prevent loss of the imide due to volatilization and the solution was analyzed by gas–liquid chromatography.

For analysis of the endothall *N*-chloroethylimide, a Micro-Tek Model 220 gas chromatograph equipped with a Coulson nitrogen detector was used. The chromatographic column, an 800 cm × 4 mm (i.d.) borosilicate glass U tube, was packed with 10% OV-17 coated on 80–100 mesh Chromosorb G (AW-DMCS). Operating temperatures for the various components were as follows: inlet, 225°; oven, 215°; transfer line, 225°; block, 240°; and pyrolysis furnace, 820°. The pyrolysis tube was fitted with a coil of nickel wire catalyst (Tracor, Inc., Austin, Tex.). Strontium hydroxide coated on an inert support was used as a scrubber. The carrier gas was helium and the reactant gas was hydrogen, with flow rates of 150 and 75 ml/min, respectively. The amounts of endothall imide in the water and hydrosoil extracts were determined from peak area measurements which were compared with those of standard endothall chloroethylimide solutions.

Analysis of Hydrosoil. Excess water was removed from the hydrosoil samples by suction filtration prior to analysis. Duplicate samples weighing 50 g each were extracted with 250 ml of acetic anhydride by stirring and boiling in a hood until the volume was reduced to about 100 ml. The soil was removed by suction filtration and the filtrate was concentrated to a volume of about 50 ml. The extract was transferred to a separatory funnel, about 30 ml of water was added, and the solution was extracted with two to four successive 25-ml portions of carbon disulfide until the CS_2 layer became clear. The CS_2 layer was discarded and the aqueous layer was extracted with three to four successive 25-ml portions of chloroform until the chloroform layer became clear. The chloroform layer was discarded and about 100 ml of glacial acetic acid was added to the aqueous layer. The solution was then concentrated to about 30 ml by heating it to a temperature of 118°. The solution was further concentrated and the endothall present in the extract was converted to its *N*-chloroethylimide derivative as described for water samples. The chloroform layer contained impurities which interfered with the detection of the imide by gas–liquid chromatography. To remove these interfering materials, the chloroform extract was swirled with 0.5 g each of attaclay and charcoal for 2 min and filtered through a dry sintered glass funnel. The filtrate was concentrated almost to dryness, dissolved in absolute methanol, and analyzed by gas chromatography as described above.

To determine the per cent recovery of endothall from the water and hydrosoil, known quantities of endothall, ranging from 0.1 to 5.0 ppm, were added to the hydrosoil and water samples. The soil was allowed to equilibrate

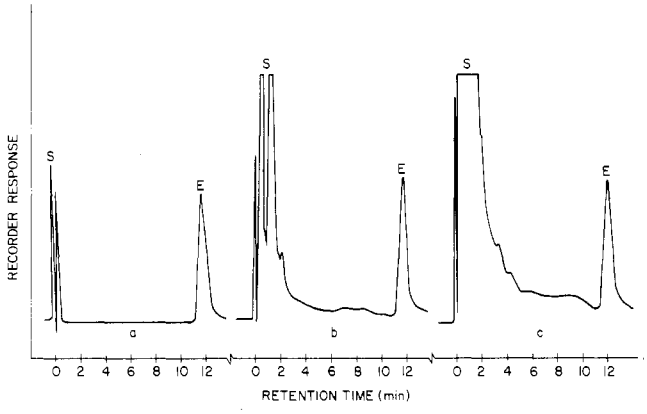

Figure 1. Gas chromatogram of: (a) standard endothall chloroethylimide; (b) and (c) endothall chloroethylimide prepared from endothall present in water and hydrosoil, respectively. S denotes the solvent and E denotes the endothall chloroethylimide.

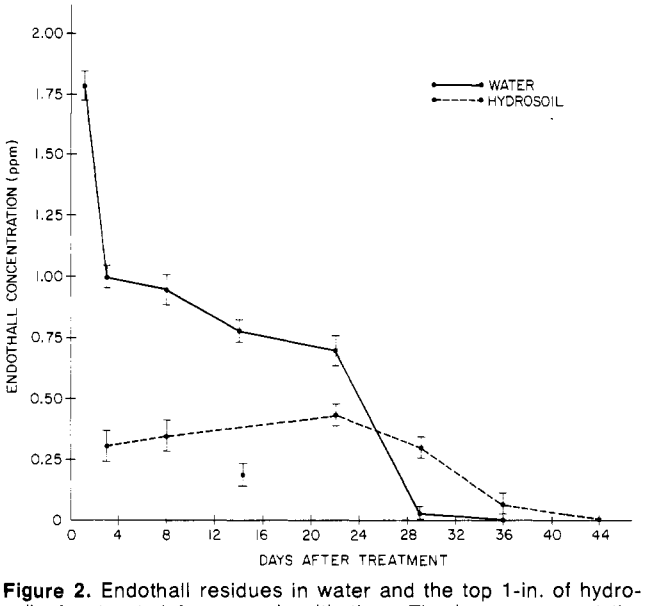

Figure 2. Endothall residues in water and the top 1-in. of hydrosoil of a treated farm pond, with time. The bars represent the range of duplicate values.

with endothall for 2–3 hr prior to analysis. The fortified samples were then carried through the entire analysis procedure. All residue data were corrected for recovery efficiency.

Persistence of [^{14}C]Endothall in Autoclaved Water and Hydrosoil. Water and hydrosoil were added to a 500-ml beaker in proportions corresponding to the ratio of water to hydrosoil in the aquaria. The beaker was covered with a petri dish and autoclaved for 30 min. [^{14}C]Endothall labeled in position 2 and 3 of the oxabicyclo ring (specific activity, 11.8 μCi/mg) was added at a rate of 2 ppm in the water and mixed thoroughly into the water phase. The amount of radioactivity in the water was measured immediately after treatment and at various intervals thereafter by adding 1-ml aliquots to 15 ml of liquid scintillation solution [5.5 g of PPO, 0.1 g of POPOP, 667 ml of toluene, and 333 ml of Triton-X (Packard Instrument Co., Downers Grove, Ill.)] and counting in a liquid scintillation counter. For analysis of radioactivity in the water, a portion of the water phase was concentrated and chromatographed on thin-layer silica gel as well as cellulose plates. The solvent systems for developing silica gel and cellulose chromatograms consisted of ethyl acetate–chloroform–formic acid (40:50:50 v/v) and ether–formic acid–water (7:2:1 v/v), respectively. After drying, the chromatograms were scanned for radioactivity in a Nuclear Chicago Actigraph.

Table I. Recovery of Endothall from Water and Hydrosoil

Fortification, ppm	No. of determinations	% recovery	
		Water	Hydrosoil
0.1	3	89 (86–94)[a]	79 (74–84)
0.5	3	87 (83–89)	78 (73–82)
1.0	3	84 (81–89)	80 (76–84)
2.0	3	90 (87–93)	72 (67–77)
5.0	3	85 (80–89)	71 (67–74)
		Avg 87	Avg 76

[a] The values in parentheses represent the range.

To determine the amount of ^{14}C in the hydrosoil, samples of hydrosoil were subjected to wet combustion (Smith *et al.*, 1964). The $^{14}CO_2$ evolved from the combusted soil was trapped in a solution consisting of monoethanolamine and 2-methoxyethanol (1:2 v/v). One-milliliter aliquots of CO_2 trapping solution were added to 15 ml of scintillation solution containing PPO, POPOP, dioxane, naphthalene, toluene, and ethanol and the radioactivity was measured in a liquid scintillation counter.

RESULTS

The gas–liquid chromatographic conditions permitted a good separation of the *N*-chloroethylimide of endothall from impurities in the soil or water extracts (Figure 1). The retention time for authentic endothall *N*-chloroethylimide was 11.7 min and the lower limit of detection of the endothall *N*-chloroethylimide was 0.03 μg. The relationship between the chromatogram peak area and the amount of endothall *N*-chloroethylimide was linear over a range of 30–6000 ng of the imide. The per cent recovery of endothall from fortified samples of water and hydrosoil is given in Table I. Recovery averaged 87% in water and 76% in hydrosoil over a concentration range of 0.1 to 5.0 ppm of endothall.

Persistence of Endothall in the Pond. The pattern of disappearance of endothall from water and hydrosoil is shown in Figure 2. The values appearing in this figure are the average of duplicate determinations. The maximum concentration of endothall in the water, 1.8 ppm, was found 1 day after treatment. A sharp drop in endothall concentration in the water occurred during the next 2 days. By this time it had decreased to about 55% of the maximum level. The decline during this period was accompanied by an increase in endothall concentration in the top 1 in. of the hydrosoil. There was a slower and steady decrease in endothall concentration in the water between 3 and 22 days following treatment. Thereafter, the herbicide concentration in the water decreased rapidly to 0.02 ppm 29 days after treatment and, after 36 days, endothall could not be detected in the water.

Except for the sample on the 14th day, the endothall concentration in the top inch of hydrosoil continued to increase up to 22 days after treatment, when it contained 0.44 ppm of the herbicide. The data on the 14th day suggest an error in sampling. The increase was rapid during the first 3 days but was gradual thereafter. The concentration of endothall in the top inch of hydrosoil began to decline after 22 days and no endothall could be detected in the top inch of hydrosoil 44 days after treatment.

Persistence of Endothall in Aquaria. The concentration of endothall in water and hydrosoil samples at various times after treatment is shown in Figure 3. The dissipation of endothall from the aquaria treated with different herbicide concentrations followed a similar pattern. The endothall concentration in the water declined rapidly during the first day following treatment. After 1 day, endothall concentration in the water of the aquaria which were

treated with 2 and 4 ppm was 80 and 86%, respectively, of the maximum level. There was a brief period of 2 days from day 1 to day 3 when the concentration of endothall in the water decreased at a relatively slower rate. After the third day, the disappearance of the herbicide continued once again at a rapid rate and endothall could not be detected in the water 7 days after treatment. As in the pond, the rate of disappearance of endothall in the hydrosoil was slower than in the water and the herbicide appeared to persist in the hydrosoil for a relatively longer period. The maximum concentration of endothall in the hydrosoil was observed 3 days after treatment. A rapid disappearance of the herbicide occurred during the next 4 days. Subsequently, the concentration of endothall in the hydrosoil decreased more gradually. After 2 weeks, endothall concentration in the hydrosoil was reduced to less than 0.1 ppm in the aquaria treated with 2 ppm of the herbicide. In the aquaria treated with 4 ppm of endothall, it took 5 weeks for the herbicide to reach a level of less than 0.1 ppm in the hydrosoil. The amount of endothall disappearing from the aquaria was observed to be roughly proportional to the amount of the herbicide applied. The bulk of endothall added to the aquarium remained in the water. During the period of the experiment, the quantity of endothall in the hydrosoil did not exceed 7% of the amount originally added.

Persistence of [^{14}C]Endothall in Autoclaved Pond Water. Thin-layer chromatographic analysis of the autoclaved pond water upon termination of the experiment (9 days after treatment) revealed that all the ^{14}C in the water was present in the form of unchanged endothall (R_f 0.48 and 0.75 on silica gel and cellulose plates, respectively). The ^{14}C in the water cochromatographed with the authentic [^{14}C]endothall. Under these conditions, 6.9% of the [^{14}C]endothall present initially (13.7×10^6 dpm) disappeared from the water within 1 day. This decrease was accompanied by the appearance of radioactivity in the hydrosoil. Subsequently, only a slight decrease occurred in the amount of [^{14}C]endothall in the water.

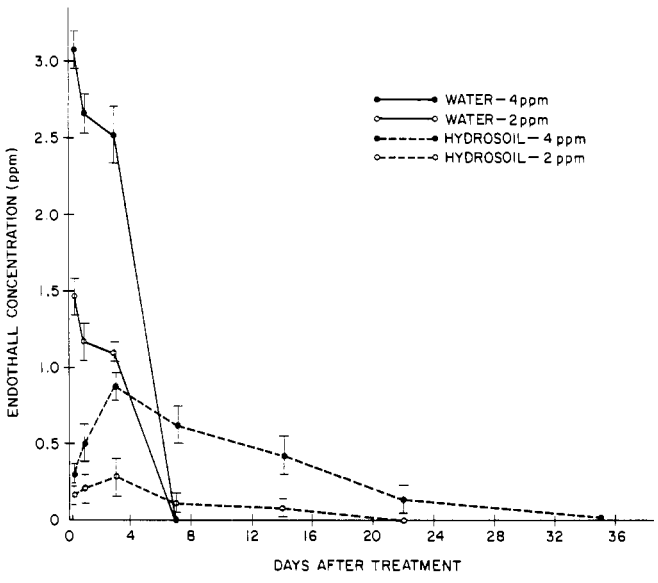

Figure 3. Endothall residues in water and hydrosoil of aquaria treated with 2 and 4 ppm of the herbicide. The bars represent the range of duplicate values.

DISCUSSION

The analytical method used for determination of endothall in this study offers various advantages over the flaxseed bioassay used by other investigators. The chemical method is direct and more precise and quantitative. The sensitivity of this method was greater than that of the bioassay technique. Using this method we were able to detect as low as 0.01 ppm of endothall in water. This method also provides a means for determination of endothall in hydrosoil which the flaxseed bioassay does not offer. By chemical assay it is possible to measure the amount of endothall in water faster than by bioassay, as the latter requires 72 hr of completion. The greater duration of the bioassay constitutes another disadvantage in that microbial degradation of the herbicide may continue during the assay period and the amount available to the test plant may then be continually decreasing.

Our studies indicate that endothall did not persist in water for an extended period. Endothall has been reported to be degraded by soil microorganisms (Jensen, 1964). Sikka and Saxena (1973) observed that aquatic microorganisms readily metabolize endothall; they isolated an *Arthrobacter* species which was capable of utilizing endothall as the sole source of carbon. Since endothall is stable in aqueous solution and its loss due to volatilization is negligible, it is assumed that microbial degradation, adsorption to hydrosoil, and possibly leaching to lower depths in the case of pond treatment are the factors primarily responsible for the disappearance of endothall from water in ponds and in aquaria.

The disappearance of endothall from water appeared to occur in three phases, both in the pond and aquarium studies. There was an initial rapid decline in endothall concentration followed by a second phase during which the loss continued at a slower rate. During the third phase, disappearance of the herbicide continued again at a relatively rapid rate. The kinetics of endothall appearance in the hydrosoil as well as the results of the [^{14}C]endothall experiment suggest that the initial decrease in endothall concentration in the water was primarily due to adsorption to the hydrosoil, while microbial degradation most probably played a major role in the disappearance of endothall in the third phase. The relatively slower decrease in endothall in the second phase may represent a lag phase during which the microorganisms capable of degrading endothall develop. Jensen (1964) observed that decomposition of endothall in previously untreated soil did not begin until after a lag period of a few weeks. He also reported that bacteria capable of degrading endothall could be isolated from soil as late as 1 year after endothall treatment, but not from untreated soil. As in the pond, a lag period was also observed in the aquarium studies, though its duration was relatively short. The aquarium studies were conducted using water and hydrosoil from a pond which had been treated 1 year before with endothall. Presumably, the microorganisms which had adapted to degrading endothall were already present when the aquaria were treated with the herbicide, thereby resulting in a shortening of the lag period and a faster disappearance of endothall. The fact that conditions were more favorable for microbial activity in the aquaria than in the field also probably contributed to a faster disappearance of endothall in the aquaria. The aquaria were maintained at a constant temperature, which was higher than in the field.

The herbicide appeared to persist in the hydrosoil for a relatively longer period than in the water. This may have been due to a number of factors, such as adsorption of endothall to the soil and, hence low availability to the soil microorganisms, lesser microbial activity due to lower oxygen levels in the hydrosoil, or different microbial populations in the hydrosoil.

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LITERATURE CITED

Frank, P. A., Comes, R. D., *Weeds* **15**, 210 (1967).
Frank, P. A., Otto, N. E., Bartley, T. R., *Weeds* **9**, 515 (1961).
Hiltibran, R. C., *Weeds* **10**, 17 (1962).
Jensen, H. L., *Acta Agr. Scand.* **14**, 193 (1964).
Pennwalt Corporation, Agricultural Chemical Division, Tacoma, Washington, personal communication, 1972.
Sikka, H. C., Saxena, J., *J. Agr. Food Chem.* **21**, 402 (1973).
Smith, G. N., Ludwig, P. D., Wright, K. C., Bauriedel, W. R., *J. Agr. Food Chem.* **12**, 172 (1964).
Walker, C. R., *Weeds* **11**, 226 (1963).
Yeo, R. R., *Weed Sci.* **18**, 282 (1970).

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Persistence of Residues of the Insecticide Phosphamidon on and in Oranges, Lemons, and Grapefruit, and on and in Orange Leaves and in Dried Citrus Pulp Cattle Feed

William E. Westlake,* Monika Ittig, Daniel E. Ott, and Francis A. Gunther

The dissipation rates of phosphamidon on and in oranges, lemons, and grapefruit were determined; the degrading deposit half-lives were 3–5 days and the persisting residue half-lives were 10–12 days. Dosages from 0.5 to 1.5 lb a.i./acre yielded maximum initial deposits of about 1.5 ppm (rind basis), which decreased to about 0.1 ppm (rind basis) after 28 days. Residues declined slightly more rapidly on leaves than on fruit. The persisting residues on all varieties of fruit and on orange leaves remained largely on the surface for as long as 28 days after application, *i.e.*, they were largely dislodgable residues. There was indication of only slight, if any, translocation into the edible portion of any of these fruits; the highest level detected was 0.02 ppm in lemon juice sacs 1 day after application. The cis isomer of phosphamidon disappeared slightly more rapidly than the trans isomer. *N*-Desethylphosphamidon was not detected in any sample (*i.e.*, <0.01 ppm). About 90% of the phosphamidon in orange rind (0.04 ppm, 14-day sample) was lost in processing the rind into dried citrus pulp cattle feed.

Phosphamidon (2-chloro-*N*,*N*-diethyl-3-hydroxycrotonamide dimethyl phosphate) is a broad spectrum systemic insecticide that has been found useful for the control of some insects and mites on citrus in Southern California. Technical grade phosphamidon is a mixture of cis and trans isomers in the proportion of 73:27 (Anliker and Beriger, 1971) plus approximately 1% each of dechlorophosphamidon (*cis-* and *trans-*) and γ-chlorophosphamidon (*cis-* and *trans-*). The cis isomers of phosphamidon and of *N*-desethylphosphamidon (a metabolite formed in plant tissues) have high biological activity, while that of the trans isomers is low.

This study was designed to obtain data on deposit and residue levels and their rates of dissipation to enable state, federal, and other regulating agencies to establish tolerances and conditions for use of the compound in the area of citrus pest control. Residue levels on and in foliage were also determined in one Valencia orange plot for comparison with similar data for fruit. Dried citrus pulp cattle feed was prepared and analyzed to determine the effect of this processing on the persisting residue levels.

Although not directly comparable due to differences in amounts applied and numbers of applications, the data reported here agree well with earlier work (Voss and Geissbühler, 1971) which showed a persisting residue half-life of 7–15 days for phosphamidon on and in oranges, compared with our 10–12 days.

EXPERIMENTAL DESIGN

Plots of mature, furrow-irrigated Valencia orange trees were sprayed with phosphamidon in April of 1971 for the purpose of determining deposit and residue dissipation rates on and in fruit and leaves and the extent of penetration into the edible part of the fruit. The compound was applied at rates of 0.5, 1.0, or 1.5 lb/acre (0.5, 1.0, or 1.5 pt of a formulation containing 8 lb of technical grade phosphamidon/gal) in 200 gal of water (plots 1, 2, and 3, respectively). Plots of furrow-irrigated grapefruit trees were sprayed in July of 1971 with 0.5 or 1.0 pt/acre and furrow-irrigated lemon trees were sprayed in April of 1972 at these same rates (plots 1 and 2, respectively, for each). All plots were replicated three times. Samples of orange fruits were collected for analysis before treatment and at intervals of 1, 3, 7, 14, 21, 28, and 42 days after treatment. Double samples were taken at the 3-, 14-, and 28-day intervals and one-half of each sample was washed in a manner simulating commercial practice before processing for analysis. Pulp (edible portion) of the fruit was analyzed at the 1-, 7-, and 21-day intervals. Leaves from plot 2 were sampled at the same intervals as fruit and analyzed for surface (dislodgable) and total (dislodgable plus penetrated) residues. At the 14- and 28-day intervals, samples of oranges were taken from plot 3 for conversion into dried citrus pulp cattle feed.

The field plot arrangement and the sampling procedure for fruit and the preparation of cattle feed prior to analysis were as described by Gunther (1969). Leaf samples consisted of 40 1-in. disks punched from the approximate centers of that number of leaves with a specially designed punch that deposited the disks in an attached 4-oz wide-mouthed jar (Gunther *et al.*, 1973). Preliminary tests showed that the calculated total leaf residues (as $\mu g/cm^2$) using the leaf-punch method agreed very well with values obtained by using the entire leaf.

Grapefruit samples were taken before spraying and at intervals of 3, 6, 10, 20, and 31 days after treatment, and lemons were sampled before spraying and at 1-, 3-, 7-, 14-, and 21-day intervals afterward. Pulp of the grapefruit

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