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When a herbicide has entered a body of water it begins to dissipate at a rate affected by the (1) water depth, (2) mean temperature, (3) rate of treatment and (4) time after treatment. In the case of moving waters, the dissipation rate can also be affected by volume dilution as a function of the surface area to the total area, and the time as a function of the rate of flow. cont

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Because of dilution, herbicide residues may be quickly elliminated from water, but residues in the bottom mud may remain for several months or longer depending on the pH of the water, the type of clay and the herbicide used.

In addition to dilution, photo, chemical and biological degradation play a large part in herbicide removal. In fact, laboratory studies show that microbial activity is the major factor involved in herbicide degradation.

Organic herbicides such as 2, 4-D are relatively nontoxic to animals, and when used properly, cause a minimum of injury to aquatic flora and fauna. Numerous feeding studies show that herbicides, are rapidly excreted in body wastes with little or no signs of accumulation in tissue. It follows that fragmentation of the herbicide molecule through metabolism can actually result in detoxification and the formation of utilizable products. In the case of 2,4-D these end products are CO2, H2O and a chloride or a terminal residue of a more complex molecule.

HERBICIDE RESIDUES
OF 2,4-D

INTRODUCTION

The addition of herbicides to water has elicited a number of environmental objections, and a plea for a moratorium on the use of these materials is often made. Organic herbicides, however, are relatively nontoxic to animals, and when used as prescribed, cause a minimum of injury to aquatic flora and fauna. Most of the uses of herbicides in aquatic situations may be described as attempts to improve the ecological state of the water. (1,2,3,12,13,14,18,19,20,24,28).

To understand both the desirable and undesirable aspects of herbicide use in water, it is necessary to know something about the residues, their disappearance or degradation, and their effects on nontarget organisms. (39). This paper discusses selected portions of the published literature dealing with the use of phenoxy herbicides in aquatic site.

Source of Herbicide Residues

Before dicussing the degradation of herbicides, some consideration should be given to the levels of residues which occur in water following the use of chemicals for weed control. The usual means by which herbicides enter water are: (1) from surface-runoff during irrigation or; (2) by application of herbicides to soil or water for control of submersed weeds in canals, ponds, or lakes; (3) by herbicide treatment of floating and emersed weeds; and (4) from treatment of banks of streams and canals for control of bank and marginal weeds.

Surface runoff - Where residues are shown to occur, the concentrations are low and persist for only short periods. Columbia Basin irrigation supply and waste waters were monitored for several pesticides during the 1961 irrigation season. Only on rare occasions small quantities of (2,4-dichlorophenoxy) acetic acid (2,4-D) were found in the supply water. Esters of 2,4-D were found more in waste drains; however, the highest level measured was 18 ppb, which was much higher then the average of all levels of 2,4-D. (9). Schulze *et at* (58), while monitoring many streams in western United States for persence of pesticides, occasionally found low levels (1ppb) of 2,4-D in the water.

Pond and lakes - Granular formulations may prevent occurrence of high concentrations of certain herbicides in water by confining portions of the chemicals at the soil (hydrosoil) surface. Granular formulations of phenoxy herbicides are notable in this respect. In a pond treated with 1.33 ppm of granular butoxyethanol ester of 2,4-D, the maximum residue level observed was 0.067 ppm. At the same time, high concentrations of both herbicides were found in the upper one inch (2.54cm) of soil. (21,25,32).

Floating weeds - In similar studies involving applications of the dimethylamine salt of 2,4-D and silvex applied at 4.5kg/ae/ha on waterhyacinth (*Eichhornia crassipes*) and alligatorweed (*Alternanthera philoxeroides*) almost all of the highest residue levels were between 1 and 0.65 ppm. The highest concentrations of herbicide did not appear in the water until 1 to 2 weeks after the treatments. This concluded that these herbicides are absorbed by the floating plants and later released into the water through roots and other submersed plant tissues. (7,8,9,33,34,35,54,55,56,57).

Marginal and ditchbank weeds - The proximity of marginal and ditchbank weeds to water almost invariably results in some herbicide entering the water following herbicide application. Principal factors affecting the amount of herbicide found in the water are: (1) treatment rate, (2) volume of water, (3) nature of the weed growth, and (4) the spray overlap at the water's edge. Considerable data with respect to residues in irrigation water following use of herbicides on canal banks were recently reported. In all but a few instances, concentrations of the herbicides in irrigation water were quite low, being under 50 ppb in most cases, despite the small size of canals involved (9,25,32,35).

Dissipation of Herbicide Residues

Dissipation in static water: Most of the herbicides registered for use in aquatic situations have water-use restrictions which require at least partial dissipation of the herbicides before normal use of the water resource is resumed. The path ways leading to dissipation are dependent largely upon the nature of the herbicides. Biological degradation accounts for much of the loss of 2,4-D. (32).

Dissipation in static water frequently requires 2-3 weeks. Averitt and Gangstad (8) found that the rate of dissipation of residues of 2,4-D (2,4-dichlorophenoxy acetic acid) at the point of application, applied for control of aquatic vegetation, was affected by the (1) rate of treament, (2) depth of water, (3) mean temperature, and (4) time after treatment. For the standard rate of treatment, i.e., 4.48 kilograms acid equivalent per hectare (kg/ae/ha) there was a decreased of 58 parts per billion (ppb) in residue for each 0.61 m increase in depth of water treated, a decrease of 115 ppb in residue for each 7-degree C increase in mean temperature, and a decrease of 53 ppb in residue for each 7-day interval of time after treatment.

A pond study was conducted to determine the uptake and dissipation of the dimenthylamine salt of (2,4-dicholorophenoxy) acetic acid (2,4-D) in water, hydrosoil and fish in ponds located in Florida and Gerogia. The residue in the treated water was dissipated to less than the negligible level of 100 ppb in 2 weeks, and did not attain this level at any time in the hydrosoil or fish flesh, from a treatment of 2.24 to 8.96 kg/ae/ha of 2,4-D (55,56,57).

Dissipation in slowing moving waters: Residue studies in Louisiana and Florida indicate that the residue of 2,4-D from spraying operations to control waterhyacinth at 2.24 -4.48 kg/ae/ha is related to (1) volume dilution as a functions of the surface area to the total area, (2) temperature in degrees C and (3) time as a function of the rate of flow or displacement (34).

Dissipation in Large Reservoirs: The use of phenoxy-type herbicides in aquatic situations is almost entirely limited to derivatives of 2,4-D. While amines of 2,4-D are commonly used for control of floating, and emergent species, esters of 2,4-D in granular form are generally applied to water infested with submersed weeds. The highest levels of 2,4-D residues in static water following the use of 2,4-D granules occurred in 8 to 15 days; trace amounts remained after 4 to 6 weeks (32,33,34,35).

Smith & Isom (60) reported maximum concentrations of 56 and 34 pmm of 2,4-D in botton mud, and 0.037 and 0.157 ppm 2,4-D in the water of two reservoirs treated at rates of 45-112 kg/ae/ha with the butoxyethanol ester of 2,4-D in granular form. Because of water movement and dilution, residues were no longer detected in water of one reservoir after 4 hr, and much reduced in the other. Residues of 2,4-D persisted in the bottom mud of the reservoirs in excess of 9 months.

Pond treatment with the PGBE ester of 2,4-D in liquid formulation resulted in lower residue levels. Dissipation from water followed the usual pattern of 4 to 6 weeks; however, at treatment rates as high as 5 and 10 ppm, no 2,4-D was detected in the soil 2 weeks after application of the herbicide. The dissipation rate of the dimethylamine salt of 2,4-D is similar to those reported for the ester derivatives. Residues of 2,4-D in water following treatment of waterhyacinth at 4.48 kg/ha and 5.60 kg/ha of the amine salt were dissipated form 0.53 and 0.97 ppm to 4 and 15 ppb, respectively, after 29 days. (4,5,6,7,8,9,10).

In Tennessee Valley Authority (TVA) milfoil studies, over 18,000 surface acres of reservoirs in Alabama and Tennessee were treated with about 170,000 gallons of dimethlamine salt of 2,4-D during April-June

1969 to control invading Eurasian watermilfoil. The DMA 2,4-D was applied at the rates of 22 and 45 kg/ae/ha of 2,4-D acid equivalent per acre. Representative habitat types were selected and monitored for 2,4-D content in water, plankton, and sediment and for plankton species composition, distribution, abundance, change, and response. The treated water had no apparent effects on most marginal plants. No harmful response to the herbicide was observed in zooplankton, phytoplankton, benthic macroinvertebrates, or fish. Water continued to be used for domestic purposes with out user complaints. Dimethlamine salt of 2,4-D appears to be noncumulative. Plankton sorbed large amounts and retained it for extended periods. Finished drinking water from municipal treatment plants on occasion contained detectable amounts of 2,4-D. (66).

Residues from Granules

Residues in water, whether applied as the ester or the acid, are generally reduced to a nondetectable level within three to four weeks. To establish this pattern under field conditions a series of relatively small ponds were treated with the granular formulation of the 2,4-D butoxeythanol ester. Seven locations in the United States and one in Canada with a total of 15 ponds were used. Of those analyzed, five at 1 ppm and two at 5 ppm, six had reached a nondetectable level by the 30th day. These ponds all behaved in a similar manner with detactable residue levels peaking between 8 and 15 days post treatment, followed by a rapid decline to the nondetactable stage. 1/

Early work done by Wilkinson (64) indicates the action of granular 2,4-D formulations in the water. Wilkinson studied several factors affecting the subaqueous rate of release from clay granules. His finding showed the following:

1. Temperature had an effect only during short periods of exposure.

2. The derivative of 2,4-D employed was the most significant factor affecting the rate of release. The rank in order of rate of release was 2,4-D acid 2,4-D BEE 2,4-D PGE 2,4-D isooctyl ester.

3. The type botton was shown to affect the total quantity of herbicide recovered. Bentonite absorbed significant quantities of herbicides.

4. pH of the water affected the rate of release of 2,4-D acid from the clay granules.

5. The type of clay and size of the granule was not a significant factor in long-term studies.

6. The quanity of the herbicide recovered was shown to depend on concentration with the 2,4-D BEE.

Data from 256 recoveries showed almost complete release from the granule by the 10th day. This substantiates the peaking factor noted in most field tests. Averitt and Gangstad (8) analyzing waters receiving

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1/ Unpublished data, Amchem Products, Inc, Ambler, Pennsylvania, 1970.

2,4-D amine treatments for water hyacinth control demonstrated a peaking at one week. Small enclosed ponds within the city of New Orleans showed almost 100 percent removal at the end of 31 days. Frank and Comes (32), reporting on a pond treated with granular 2,4-D butoxyethanol ester at a rate of 1.3 ppm, commented on the low peaking level of 0.067 which occured between 12 an 18 days. This was approximately 1/3 of the calculated conentration. The hydrosoil showed a much higher initial concentration with a greater persistence lasting to 55 days before a nondetectable level was reached as opposed to the 24-day residual in the water.

More recent work by Steward and Nelson (62) supports the pattern of peaking and rapid decline which is being established. They compared polyvinyl chloride controlled release pellets with the attaclay. Granular formulation of the butoxyethanol ester of 2,4-D in plastic enclosures having a mud base and a fairly dense weed population. The data from the two concentrations, 1 and 2 ppm, peak out between 7 and 14 days and the nondetectable level was reached between the 2nd and 4th week.

Residues in Fish and Shellfish

Rodgers and Stallings (51), using the standardized techniques, noted that maximum whole body and tissue residues of 2,4-D were related to the concentration of the ester and that they declined as the ester was hydrolyzed. The rapid uptake may result from increased solubility of 2,4-D ester across the gill membrane. Absorption of the ester by the lipid and lipoprotein in the blood may enhance the distribution of 2,4-D to various organs. In summary, they note that the maximum residue levels were observed in most organs of fed fish within 1 to 2 hours exposure and within 1 to 8 hours for the starved fish. After maximum residue levels, 19.5 ug/g for catfish and 54.6 ug/g for bluegills, were reached, the herbicide or its metabolite was eliminated rapidly.

Whitney et al (63) in North Carolina, carrying out biological studies in conjuction with a 2,4-D butoxyethanol ester treatment for milfoil control in Currituck Sound, sampled fish over a 3-week period. Of 39 samples, the highest concentration detected was 0.24 ppm found in a largemouth bass 8 days following application. Of the six fish species, pumpkinseed sunfish, white and yellow perch, catfish, largemouth bass, and bluegill sunfish, no one specie appeared to collect more residue than the other. Twenty-six of the 39 samples showed on residue, while the remaining samples had less than 0.2 ppm, except for one bass which contained 0.24 ppm.

Rawls (44,45,46,47,48,49,50) working with the problem of residues in oysters in the Chesapeake Bay area, comments in his final report "crabs, fish, clams, and oyster will accumulate and lose 2,4-D butoxyethanol ester residues in varying amounts depending on the bioassay animals, the distance they are held from the treated area, water movement through the study plots, and the degree of vegetation within and around the sites of herbicidal application." He further notes that clams and oysters acquire greater residues than do fish and crabs. Residue peaks are reached from 1 to 9 days following application and rapidly decline thereafter. The real question of residues found in aquatic animals lies in the probability of continuous exposure and the animals' ability to take certain actions to avoid residue buildups. Crabs and fish can readily move out of treatment areas while oysters and other bivalves have the ability to flush out toxic compounds as the dosage levels decline.

Wilkinson (64) included 30 posttreatment and one pretreatment samples of benthic organisms among those analyzed for 2,4-D butoxyethanol ester. The highest concentration, 0.23 ppm, was recorded in a sample collected on day after treatment. Twelve samples showed very slight residues, and the remainder no residues. Blue crabs at no time showed any residues.

Water Use

The use of herbicides in water assumes that in the normal process of degradation certain amounts may deposit on the bottom muds. The use of rapidly sinking granular formulations thus increases the probability that residues can be found in the bottom muds. Frank and Comes (32) indicated that greater residues of 2,4-D butoxyethanol ester were found in the hydrosoil than in the water, Smith and Isom (60) indicated high levels in the muds following treatment. These residues were detected up to 10 months at Watts Bar and 9 months at Guntersville, Alabama. Wilson (65) also found residues in the muds and was concerned about the erratic pattern.

Residues in Irrigation Water: Bruns (15) made the following statement after irrigating red Mexican beans with 2,4-D-treated water. "The response of red Mexican beans to field applications of 2,4-D at 2.24 to 6.66 kg/ae/ha in irrigated water during the seedling and bloom stages of growth was studied."

"The application of 2.24 kg/ae/ha 2,4-D in irrigation water during the seedling stage caused pronounced injury to the top growth and roots of the bean plants. However, within 16 days after the application, plants began to recover and no significant reduction in yield resulted."

"The rate of 6.6 kg/ae/ha of 2,4-D during the seedling stage caused severe damage to the top growth and destroyed nearly all of the root systems of the plants. Amazingly, within 3 weeks, a number of plants began to recover with the development of club-like adventitious roots.

"Application of 2.24 and 6.72 kg/ae/ha of 2,4-D in irrigation water during the bloom stage caused some leaf chlorosis and damage to the root systems and hastened somewhat the maturity of the bean plants. The 2.24 kg/ae/ha treatments caused no significant reduction in yield, but the 6.72 kg/ae/ha applications reduced the yield 29 percent."

"Laboratory and greenhouse tests exhibited no carry-over effects of 2,4-D in bean seeds harvested from treated plots."

A second phase of Bruns' (15) work indicated that:

"1. The rates of 2.24, 4.48, 8.96 and 17.92 kg/ae/ha were lethal to 13, 22, 65, 54 percent of the plants, respectively, whereas lesser rates caused no death of plants."

"2. Root systems of injured plants were partially or completely destroyed. Remaining portions of fragments showed varying degrees of discoloration and of tip enlargement. Depth, distribution, and development of the root systems at time of treatment apparently was an important factor in the experiment."

Residues in Potable Water: Potable water supplies frequently become infested with algal blooms which produce objectionable flavors and ordors. These may become offensive enough to make the water unfit for consumption. Copper sulfate has been used for many years to prevent occurrence of such growths, and at the present time, is the only herbicide used to any extent in potable water. Another caused of flavors and ordors in water is the death and decay of large masses of vascular aquatic weeds. The ensuing anerobic conditions produce hydrogen sulfide and other substances typical of stagnant water.

There have been relatively few instances of undesirable flavor from herbicides used in drinking water. During 1966, the Tennessee Valley Authority used large-scale applications of granular butoxyethanol ester of 2,4-D at rates of 44 to 112 kg/ae/ha for control of Eurasion watermilfoil. The highest concentration of 2,4-D recorded at any of the water-treatment plants downstream where water was monitored was 2 ppb (60,66). In the United States the combined permissible level of phenoxy-type herbicides in potable water sources is 0.1 ppm.

Residure in Fish and Wildlife Management: The use of herbicides as tools in fish and wildfish management is becoming more important each year. Whitney et al (63) have pointed outthat weed control is a major phase of fish management in over a million acres of ponds in southern United States. In recent years, Florida alone has seen the construction of more than 4,000 farm ponds, and during the 20 years preceding 1965, over 1.25 million ponds plus numerous other water retaining structures, were built by the Soil Conservation Districts throughout the United States. Fishing and other recreational activities in many of these waters, especially those of the southern states, would be impossible without some form of chemical weed control. An average cost of $10/ha for weed control was considered acceptable in 1964. In some regions of the united States, notably the eastern and southeastern states, large areas of weed growth have eliminated almost entirely the harvest of fish and waterfowl. The harvest of oysters (Crassotrea virginica), clams (Mya arenaria), and crabs (Callinectes sapidus) in certain estuarine water long noted for production of seafood, is being restricted by weed species such as watermilfoil and eelgrass (Zostera marina L.) The use of 2,4-D for control of undesirable weeds in tidal areas opens the water to commerical and sport fishing and releases from competition the native plants which attract waterfowl. Maintenance of the extensive and valuable areas of water and marsh would be impossible without aquatic herbicides. (7,10,16,17,18,19,20,21,22,23,24,29).

Residues in Mammals: Chronic or acute toxicity of aquatic herbicides in water to humans, livestock, and wildlife are obvious but perhaps overemphasized dangers. Most organic herbicides are plant toxicants and have little or no effect on animals except in the statement was recently made that "to date, no reported example has been found of toxicity in livestock due to pesticides or herbicide contaminants of water supplies in general". Cases of acute poisoning have been accidental and due to drinking by livestock from left over herbicide solutions. Where herbicides are used in water with due regard to the welfare of fish, there is little danger of livestock poisoning. Because of the lower tolerance levels for fish than for livestock, the presence of live fish is ample evidence that the water is safe for livestock. Numerous feeding studies show that herbicides, unlike certain insecticides, are rapidly excreted in body wastes with little or no accumulation in tissue. Where residues were found in body tissues, or in milk, they persisted for very short periods, usually not more than several days. Persuasive evidence was presented to show the wide margin of safety involved in the use of herbicides at concentrations normally applied for weed control. (25,26,27,37,38,39,43)

Residue studies and observations are reported of the effects of herbicides on phytoplankton and invertebrate funa (10,17,19,26,25,43,58). Where the aquatic biota have been effected, the common pattern observed has been: (1) the death of macrophytes and a reduction in number of phytoplankton; (2) a loss in the number of insects associated with the rooted plants; (3) a decrease in the microfauna population; (4) an increase in density of phytoplankton; (5) and finally, and increase in population of various forms of aquatic fauna. The time required for this sequence of events varied, but most studies reported periods of 2 to 3 weeks. Death and decay of the rooted plants created a nutrient-enriched environment ideal for the growth of phytoplankton that serve as the basic link in the aquatic food chain. Only in rare cases were overall effects detrimental to fish-food organisms or fish production. Rawls (45) has suggested that where fish-food organisms and botton-dwelling invertebrates were adversely effected, the problem was linked directly to anerobiosis in the immediate environment.

Degradation of Herbicides

Pathways of herbicide degradation in the aquatic environment (photo, chemical, and biological) presumably are similar to the pathways involved in degradation of herbicides in the terrestrial environment. Specific modes of degradation, however, may be significantly different. Whereas terrestrial degradation occurs predominantly in an aerobic medium, the aquatic environment, particularly beneath the water-soil interface, is largely deficient in oxygen. The microbe populations, their metabolic processes, and the end products of metabolism should be expected to vary widely from the aerobic forms. All degradation processes may occur at rates which differ greatly from those which take place in the familiar terrestrial environment. (30,31-40,41,42,52,53).

Photodegradation: Solutions of 2,4-dichlorophenol (DCP), sodium salt of 2,4-D, and butyl and isopropyl esters of 2,4-D irradiated with ultraviolet light from a 660-watt mercury discharge lamp. Degradation of all compounds was relatively rapid and pH dependent. DCP was decomposed most rapidly, with 50 per cent decomposition of 0.26 millimolar solutions occurring in 5 min at pH 7. Similar solutions of the sodium salt, butyl, and isopropyl drivatives of 2,4-D were 50 per cent degraded in 71, 54, and 48 min, respectively. In all cases, degradation proceeded more rapidly as the pH of solutions increased. Despite these results, it was concluded that ultraviolet energy from sunlight would not effectively decompose 2,4-D in natural waters. (5,6,11, 25).

Chemical degradation: Most organic herbicides used for control of aquatic weeds are resistant to chemical attack. While herbicides, such as the phenoxyalkanoic acids, are rapidly converted to salts; and ester derivatives are hydrolyzed to acids, the basic herbicide molecules are quite stable. During studies on the kinetics of degradation of the PGBE ester of silvex, were unable to degrade this herbicide to 2,4,5-trichlorophenol by reacting solutions with varying concentrations of HCl or NaOH. Neither chlorine nor $KMnO_4$ were effective in removing 2,4-D or ester derivative from surface waters; however, either treatment successfully removed the closely related DCP (4,5,6,21,27,36).

Biological degradation: Among the agents of biological degradation are the various forms of aquatic fauna, flora, and the microbial population. All major groups of fauna present in water containing a herbicide are found to have some residue of the chemical. Whether the eventual loss of herbicides from these organisms is due to metabolism or to excretion of the unaltered compound to the surrounding medium is a basic question. The large volume of water, compared to the total mass of animal life in a natural body of water makes it unlikely that degradation by aquatic fauna plays a major role in reduction of herbicide levels. (35,36,66).

Labortory studies show that microbial activity is the major factor involved in degradation of herbicides in natural water. Aly and Faust (5,6) observed that 2,4-D in lake water alone was not degraded during a period of 120 days. However, by "seeding" 20 ppm solutions of 2,4-D with lake mud, total degradation of 2,4-D occurred in 65 days. Successive additions of 2,4-D to the same media resulted in shorter periods required for complete degradation of the herbicide. Adapted populations of microorganisms were capable of degrading 81 to 85 per cent of the 2,4-D in 24 hr. Using mud from a lake treated with 2,4-D the previous year, the initial addition of 2,4-D was decomposed in about 35 days. The adapted organisms were capable of persisting in the lake mud for an extended period. Hemmett and Faust (36) in a study of the biodegradation kinetics of 2,4-D observed that three variables must be considered: (1) microorganism concentration, (2) substrate concentration, and (3) ratio of microorganism concentration to substrate concentration. These three variables affect the rate at which 2,4-D is converted to carbon dioxide, water, and hydrochloric acid.

The biodegradation appeared to follow zero-order kinetics, with the oxidation rate independent of the substrate concentration. When the ratio of microorganism concentration to 2,4-D concentration was held constant, constant rates of oxidation were observed which suggested the enzyme systems were saturated with substrate. Thus, substrate concentration was not a limiting factor in these kinetic studies, further substantiating the zero-order kinetic model. Acclimatization time also appeared as a factor. The longer the period of acclimatization, the shorter was the period of time to effect "ultimate" biodegradation of 2,4-D. In a mixed culture, chloro phenoxy intermediates were not detected.

Uptake and Metabolism

The uptake and metabolism of phenoxy herbicides has been studied for the past three decades. (40,41,42). The herbicide 2,4-D is excreated very nearly 100 percent by the animal body (39, 43) as the parent acid or a detoxified chemical and there are no apparent detrimental effects at the levels used in commerical agriculture. In plants, there are specific metabolites related to a particular plant species (40,41,42).

Rodger and Stallings (51), studying the dynamics of 14-C labeled 2,4-D butoxyethanol ester in organs of rainbow trout, channel catfish, and bluegills, noted difference in the hydrolysis rate in aquariums with and without fish. Without fish, 40 hours were required to degrade 50 percent of a 1.0 mg/l solution of the 2,4-D butoxyethanol ester. With 1.5 g/l of fish present, the same amount of chemical was hydrolyzed in 3 hours. At the end of 24 hours, 0.01 mg/l remained as opposed to 0.5 mg/l after 90 hours in the water without fish. Although the ratio of fish to total water would be considerably higher than the maximum standing crop, it can be assumed that the presence of fish will aid in a more rapid hydrolysis in the field.

Schultz (55) studied the uptake and dissipation of 2,4-D amine salt in fish in growth pools. He found that the herbicide was rapidly dissipated but residues of 14-C Carbon were subsequently determined in the muscle tissues of the fish flesh. It was postulated that the herbicides excreted by the fish were degraded by microflora of the growth pool and were resorbed as radio active carbon dioxide fragments. Sikka _et al_ (59) demonstrated that this was indeed the case.

The growth pool studies by Schultz were repeated by Stallings and Huckins (61). They demonstrated that the radio active carbon dioxide fragments were incorporated into the fatty acids of the fish flesh and that these residues are not the parent herbicide _per se_.

Environmental Aspects

Biological transformation of chemical residues involves a variety of intermediate substances until one or more final end products are obtained. In the case of 2,4-D these end products are carbon dioxide, water, and a chloride ion or a terminal residue of a more complex configuration.

The process of cometabolism is recognized as an important mechanism of metabolism for certain phenoxy herbicides. The principal reactions associated with the metabolism of 2,4-D include dealkylation, dehalogenation, amide or ester hydrolysis, oxidation, reduction, aromatic ring hydroxylation, ring cleavage, and condensate or conjugate formation. Detoxication and excretion are the ultimate results of 2,4-D ingestion by animals and fish. The formation of glycosides and glucuronides by many organisms constitutes a mechanism for detoxication. The glycosides and glucuronides are generally more water soluble than the parent herbicide molecule and are therefore more readily excretable by living organisms.

Many organisms obtain energy for other life processes in the metabolism of 2,4-D. The initial metabolic reactions require an expenditure of energy by the organism. Only when the herbicide is fragmented into compounds that can be channeled into oxidative cycles (e.g., the Krebs cycle) does the organism derive useful energy. The complete oxidation of a chemical to carbon dioxide and water, although perhaps desirable from a "complete degradation" point of view, may be a wasteful process. Actually by a series of intermediate processes the energy originally incorporated into chemical bonds in herbicides may be transferred into ecologically acceptable products that can be used benefically by many organisms when needed. Thus the overall trend in herbicide metabolism is toward less complex molecules. It follows that fragmentation of the molecule through metabolism generally results in detoxication and the formation of utilizable products. This is exemplified by the ultimate degradation of 2,4-D to alanine and succinic acid. This represents the ultimate conversion to an ecologically acceptable metabolite.

Only in a few instances are the toxicological properties of one or more of the metabolites fully known. Although the general trend of herbicide metabolism is toward increasingly less toxic molecules, in some instances the toxicity of the metabolite may be equal to or greater than that of the parent pesticide molecule. Some pesticides, such as the herbicide sesone and probably 2,4 DEP, MCPES, and 2,4-DEB, are not biologically active themselves but actually require metabolic hydrolysis for activation to a phytotoxicant. In nearly all cases, however, even the more toxic metabolite is ultimately degradable to an ecologically acceptable entity.

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