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LITERATURE REVIEW OF THE ENVIRONMENTAL FATE OF FOUR HERBICIDES APPLIED TO SURFACE-WATER BODIES IN NEW JERSEY

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by Jacob Gibs

ABSTRACT

Four of the most frequently used organic herbicides applied to surface-water bodies in New Jersey are diquat, endothall, fluridone, and glyphosate. These four herbicides are used primarily to control rooted vegetation in lakes, impoundments, and other surface-water bodies with low water velocities. In 1994, the active ingredients in the four herbicides were applied to the surface area of water bodies in New Jersey as follows: diquat, 3,720 pounds (1,688 kilograms) was applied to 2,643 acres (1,070 hectares); endothall, 3,920 pounds (1,778 kilograms) was applied to 408 acres (165 hectares); fluridone, 160 pounds (73 kilograms) was applied to 1,082 acres (438 hectares); and glyphosate, 590 pounds (268 kilograms) was applied to 220 acres (89 hectares). Each of the four organic compounds has different modes of herbicidal action and different behaviors in the aquatic environment, resulting in different application constraints or variables to achieve effective control of nuisance vegetation. The variables include target plant or plants; amount of active ingredient per application; application method and formulation; and season, time of day, and weather conditions required for application.

The available body of information concerning the environmental fate and possible modes of transport of diquat, endothall, fluridone, and glyphosate is described, and the sources are listed. This information can be used to determine whether the herbicide is being applied in a manner that is effective, minimizes exposure to the users of the treated water, and prevents unintended changes to the aquatic environment. Environmental fate studies conducted under controlled laboratory conditions, environmental fate and transport studies conducted on site, and numerical simulations of field applications or controlled laboratory studies are included. The literature reviewed in this report was published during 1960-95; literature published during 1980-95 is emphasized.

INTRODUCTION

Four of the most frequently used organic herbicides applied to surface-water bodies in New Jersey are diquat, endothall, fluridone and glyphosate. These four herbicides are used primarily to control rooted vegetation in lakes, impoundments, and other surface-water bodies with low water velocities. In 1994, the number of pounds of active ingredients for each herbicide were applied to the surface area of water bodies in New Jersey as follows: diquat, 3,720 pounds (1,688 kilograms) was applied to 2,643 acres (1,070 hectares); endothall, 3,920 pounds (1,778 kilograms) was applied to 408 acres (165 hectares); fluridone, 160 pounds (73 kilograms) was applied to 1,082 acres (438 hectares); and glyphosate, 590 pounds (268 kilograms) was applied to 220 acres (89 hectares) (Sherry Driber, New Jersey Department of Environmental Protection, written commun., 1997). (In this report, the units are those used in the original literature.) Each of the four organic compounds has different modes of herbicidal action and different behaviors in the aquatic environment, resulting in different application constraints or variables to achieve effective control of nuisance vegetation. The variables include target plant or plants; amount of active ingredient per

application; application method and formulation; and season, time of day, and weather conditions required for application.

The State of New Jersey regulates the application of pesticides to surface-water bodies to control nuisance vegetation (weeds and algae) and insects through the Aquatic Pesticide Permit (APP) program. The APP includes requirements which assure that the pesticides are used properly and that potentially unacceptable results, such as adverse effects to users and aquatic organisms of the treated water body and its downstream reaches, are avoided while still providing effective control of aquatic vegetation or insects (Sherry Driber, New Jersey Department of Environmental Protection, written commun., 1997).

An APP is issued to a licensed applicator for a full growing season or less and allows for the use of as many as three different pesticides. The APP includes the water-body name, location, acreage, and average depth; pesticides name(s), dosage rate, treatment dates, and areal extent of each treatment; uses of the water body and location of the uses; location of any shallow wells near the shoreline of the water-body; and restrictions on the uses of the water body and its downstream reaches and withdrawals from any shallow wells located near the shoreline following treatment.

The number of APP's issued has increased steadily. In 1994,1995, and 1996, the number of APP's issued was 671, 721, and 776, respectively. Over this 3-year period, the number of APP's increased 15.6 percent. Approximately 700 surface-water bodies located in New Jersey were treated with herbicides in 1996. Multiple permits can be issued for each surface-water body (Sherry Driber, New Jersey Department of Environmental Protection, written commun., 1997). This explains the difference between the number of permits issued and the number of water bodies treated.

Each APP and related set of requirements are evaluated by the State of New Jersey. In order to accomplish a timely evaluation, information about the environmental fate and transport of diquat, endothall, fluridone, and glyphosate is needed in a concise and easily usable format. This information can be used by water-resource planners to determine whether the herbicides are being applied in a manner that is effective, minimizes exposure to users of the treated water, and prevents unintended changes in the aquatic environment.

This report describes the available body of information concerning the environmental fate and possible modes of transport of diquat, endothall, fluridone, and glyphosate and lists the sources. Environmental fate studies conducted under controlled laboratory conditions, environmental fate and transport studies conducted on site, and numerical simulations of field applications or controlled laboratory studies are discussed. The literature reviewed in this report was published during 1960-95; literature published during 1980-95 is emphasized.

DIQUAT

Diquat (6,7 - dihydrodipyrido[1,2 - α:2',1' - c] pyrazinedium ion) is a dipyridylium compound related to quaternary ammonium compounds (Crafts, 1975). Diquat formulations are aqueous solutions of the bromine salt (Reinert and Rodgers, 1987).

Application Methods and Mode of Action on Susceptible Plants

Diquat controls many submerged aquatic macrophytes (rooted plants) and some types of filamentous algae in static and low turbidity waters (Klingman and others, 1975). Diquat is a quick-acting contact herbicide used in a nonselective manner; that is, it affects all plants (Simsiman and Chesters, 1976). It acts either as a systemic or contact herbicide, depending on the extent of absorption into and translocation within the plants being treated (Simsiman and others, 1976). Turbid or muddy water substantially reduces the effectiveness because diquat strongly binds with or adsorbs onto suspended particles (Klingman and others, 1975). Hardness also reduces the effectiveness of diquat because calcium ions are thought to be antagonistic (Murphy and Barrett, 1990).

Normal application to static or slowly moving water consists of 0.5 to 1 milligram per liter (0.47×10^{-5} to 0.931×10^{-5} ounces per gallon) of active ingredient during the active growing phase to kill submerged weeds and 1.0 kilogram of active ingredient per hectare (0.892 pounds per acre) to kill many floating and emergent aquatic macrophytes (Murphy and Barrett, 1990; Newbold, 1975). Diquat is most effective in the early part of the growing season when plants are actively photosynthesizing and the tissues are soft and easily decomposed. Diquat is particularly effective against non-rooted species and those that do not have underground rhizomes or storage organs (Murphy and Barrett, 1990).

A complete weed die-off occurred 10 days after the application of 4 pounds per acre (3.57 kilograms per hectare) of diquat to two lakes in western New York State (Sewell, 1970). Diquat achieved a complete weed kill 4 days after treatment at 5 parts per million to a weed-infested simulated aquatic system (Coats and others, 1964). Application to a flowing stream at a rate of 20 to 28 parts per million controlled all submerged plants, primarily sago pondweed and speedwell, in the area of application for 6 to 8 weeks after each treatment at drainage ditch 5-D near Kennewick, Washington. Two pounds of diquat cation per cubic foot per second of streamflow equals 26.7 parts per million instream concentration per second. One gallon of Ortho Diquat 2[1] spray or Ortho Diquat Water Weed Killer contains 2 pounds of diquat cation (Stanley and Gangstad, 1987).

Diquat is, as are other dipyridylium compounds, susceptible to reduction and forms a water-soluble, stable free radical, which is the source of the phytotoxicity (toxicity to plants). Photosynthesis, particularly the light reaction component of photosynthesis, has an important role in the reduction of diquat and the resulting herbicidal activity (Mees, 1960). Simsiman and Chesters (1976) hypothesized that the accumulation of hydrogen peroxide formed during re-oxidation of the free radical of diquat (reduced diquat) is the most plausible cause for the herbicidal mode of action of diquat.

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[1]The use of brand names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

Methods of Analysis

Extraction, Concentration, and Removal of Analytical Interferences

Diquat is a highly polar, cationic herbicide that is not reproducibly extracted with water-immiscible organic solvents, but is stable in mineral acid (Simsiman and others, 1976). Diquat can be extracted from various solid and semi-solid materials, and analytical interferences can be removed by refluxing in acid (Frank and Comes, 1967; Simsiman and Chesters, 1976); however, the extraction of diquat from water samples does not require refluxing in acid. Concentration and removal of interferences of diquat in water are accomplished by passing a filtered water sample through cation exchange resin, followed by elution with a saturated solution of ammonium chloride (see table 1). Cation exchange resin does not remove analytical interferences for highly colored water extracts: therefore, additional sample extract processing steps may be needed (Simsiman and Chesters, 1976). Faust and Hunter (1965) used anion exchange resin to remove colored materials from lake-water samples; 100 percent recoveries were reported, but no concentration of diquat occurred after passing the sample through the anion exchange resin.

Determination and Identification

The methods used for determination of diquat in water are light absorption ultra-violet (UV) spectrophotometry and gas chromatography (Simsiman and others, 1976).Two UV spectrophotometry analysis methods have been developed for the detection of diquat. The reduced form of diquat exhibits an absorption peak at 379 nanometers, and quantitative measurements are performed near this wavelength (table 1). Sodium thiosulfate is used to reduce diquat. The detection limits were as low as 1 to 50 micrograms per liter in water, as determined by Frank and Comes (1967) and Faust and Hunter (1976), respectively. Recoveries ranged from 90 to 104 percent (Faust and Hunter, 1965) and 70 to 80 percent (Grzenda and others, 1966) in water. The unreduced form of diquat exhibits peak absorption at 310 nanometers. UV absorption spectroscopy at this wavelength is specific and suitable for determining diquat concentrations (table1). Quantitative recoveries, approximately 100 percent, of unreduced diquat in water samples were comparable to those of the sodium thiosulfate reduction method (Yuen and others, 1967). Relatively clean water samples with high concentrations of unreduced diquat (1 milligrams per liter or greater) can be analyzed directly by UV absorbance at 310 nanometers without preconcentration steps of ion exchange or evaporation (Hiltibran and others, 1972).

Gas chromatography with a flame ionization detector can be used to quantitate diquat in aqueous solution. Gas chromatography of fortified samples was performed by Soderquist and Crosby (1972) by first subjecting the sample to direct catalytic hydrogenation (table 1). Soderquist and Crosby (1972) produced a detection limit of 0.1 milligram per liter and a recovery of 36 to 43 percent.

Table 1. Techniques for extraction, removal of interferences, and determination of diquat in sediment and water

[N, normality; UV spec, ultraviolet spectrophotometry; GC, gas chromatography; hr, hour; g, gram; mL, milliliter; mg/L, milligrams per liter; mg/Kg, milligrams per kilogram; µg/L, micrograms per liter; --, not applicable; <, less than; FID, flame ionization detector]

Sample type	Concentration range of samples analyzed	Sample size	Extractant	Extraction technique	Cleanup method	Method of determination	Detection limit	Recovery (percent)	Reference
Sediment	--	--	18N H_2SO_4	Reflux, 5 hr	Cation exchange at pH 9	UV spec, reduced	--	32	Frank and Comes, 1967
Sediment	130 mg/kg	7.6 g	18N H_2SO_4	Reflux, 5 hr	Cation exchange	Radioactivity	--	66 -73	Simsiman and Chesters, 1976
Water	1.0 -10 mg/L	--	--	--	Anion exchange	UV spec, unreduced	50 µg/L	100 -103	Faust and Hunter, 1965
Water	1.0 mg/L	500 mL	Cation exchange	--	Cation exchange	UV spec, unreduced	--	94	Simsiman and Chesters, 1976
Water	3.3 - 0.01 mg/L	--	Cation exchange	--	Cation exchange	UV spec, reduced	10 µg/L	70 - 80	Grzenda and others, 1966
Water	0.62 - 0.01 mg/L	--	Cation exchange	--	Cation exchange	UV spec, reduced	1 µg/L	88	Frank and Comes, 1967
Water	0.1 -1.0 mg/L	100 mL	--	--	--	GC, FID	<0.1 mg/L	36 - 43	Soderquist and Crosby, 1972

Fate in Aquatic Systems

When diquat enters the water environment, it is subjected to various chemical, microbiologically mediated, and physical environmental-fate processes. These processes interact both simultaneously and sequentially. Some environmental processes are assumed to be in equilibrium, such as partitioning, which implies that they are reversible. Other processes, such as oxidation/reduction, are assumed to be irreversible. The chemical and physical properties, environmental degradation-rate constants, and partition coefficients are shown in table 2.

Table 2. Physical and chemical characteristics or properties of diquat

[°C, degrees Celsius; <, less than; --, not applicable]

Chemical and physical characteristics or properties	Description or value	Reference
Type of organic compound	Bipyridylium	Crafts, 1975
Empirical formulae		Stanley and Gangstad, 1987
Cation	$C_{12}H_{12}N_2$	
Dibromide	$C_{12}H_{12}N_2Br_2$	
Melting point, °C	340	Petit and others, 1995
Solubility in water, grams per liter	700	Petit and others, 1995; Budavari and others, 1989
Henry's law coefficient, atmospheres meter^3/ mole	Very small	Reinert and Rodgers, 1987
Bioconcentration factor, dimensionless	<1 - 62	Petit and others, 1995
Octanol-water partition coefficient, dimensionless	603	Reinert, 1989
Mode of degradation in water		
Photolysis half-life, days	2 - 11	Petit and others, 1995
Hydrolysis half-life, days	Very long, no significant hydrolysis	Reinert and Rodgers, 1987
Biodegradation half-life, aerobic, days	<15 to 32	Petit and others, 1995
Biodegradation half-life, anaerobic, days	50	Simsiman and Chesters, 1976
Sorption partition coefficient (K_d), dimensionless		
Soils	708 - 2863	Petit and others, 1995
Montmorillonite	21 - 57	Petit and others, 1995
Organic carbon (K_{oc})	205	Reinert and Rodgers, 1987
	690	Reinert, 1989

Partitioning

Volatilization

Diquat is highly soluble in water, does not have a measurable vapor pressure (Weed Science Society of America, 1983), and therefore, does not significantly partition into the vapor phase from aqueous solution (table 2).

Sorption

The water solubility of diquat is 700 grams per liter (table 2). On the basis of this solubility, a low tendency to sorb to particles is expected. Many studies, however, have shown a strong affinity for or binding of diquat to sediment. For example, 80 to 99 percent of the diquat applied was found on suspended solids and sediment (Simsiman and Chesters, 1976). Sorption of a cationic herbicide, such as diquat, is dependent on the aquatic system pH and ionic strength (Reinert, 1989). The extent of sorption on humic acids depends on the stability of the humic acid-diquat cation complex (Reinert, 1989).

Diquat is tightly bound to clay interlayer spacings because large cations, such as diquat, displace smaller inorganic cations, such as sodium (Weber, 1972). Khan (1974) determined that the primary sorption mechanism for diquat on clay particles is ion exchange with some charge transfer processes occurring. Diquat is adsorbed by montmorillonite and kaolinite in direct proportion to the cation exchange capacity and is not easily exchanged (Pionke and Chesters, 1973). Weber (1972) and Simsiman and others (1976) hypothesized that diquat is not bioavailable, and Eisler (1990) hypothesized that diquat is not biodegradable when sorbed to soils. The extent of sorption on humic acids depends on the stability of the humic acid-diquat cation complex (Reinert, 1989).

Birmingham and Colman (1983) determined that the diquat sorption capacity of fresh water algae and *Myriophyllum spicatum* (Eurasian watermilfoil) ranged from 0.6 to 2.4 milligrams per gram dry plant weight and that 40 to 70 percent of the sorbed diquat was loosely bound, which is defined as desorption by a 5 molar ammonium chloride solution. The sorption capacity of a soil with 22.7 percent organic carbon was approximately 2.5 milligrams per gram dry soil weight, and approximately 35 percent of the sorbed diquat was loosely bound. Residual plant toxicity in a closed system was determined to occur at 7 percent of the diquat sorption capacity of the soil.

Frank and Comes (1967) found that 0.62 micrograms per milliliter of diquat disappeared rapidly from water in ponds within 4 days, but was not detected in pond sediment until the 24th day after treatment. The concentration of diquat reached a maximum on the 56th day. The data from Frank and Comes (1967) also show that a large percentage of diquat is sorbed by weeds, is not degraded, and is not found in sediment until the dead weeds settle and decompose at the sediment-water interface. The herbicide probably will be associated with the organic layer until diffusion onto clay particles or a mixing of the organic and inorganic particles takes place (Simsiman and others, 1976).

Degradation

Biologically mediated reactions

Microbial degradation is one of the major aquatic-fate processes affecting diquat persistence (Simsiman and others, 1976).

In plants.--Aquatic weed species, such as alligator weed, elodea, sago pond weed, and American pond weed, absorbed root or foliar-applied diquat (Funderburk and Lawrence, 1964; Davies and Seaman, 1968; Hiltibran and others, 1972). Little or no translocation was observed during daylight periods for susceptible plants.

Studies indicate that diquat is not degraded in higher plants that are susceptible to this herbicide. Autoradiographs of thin layer chromatograms of extracts from alligator weed indicated that the only ^{14}C- labeled material in the extract was diquat (Funderburk and Lawrence, 1964). An in vitro study of diquat metabolism using ^{14}C- labeled diquat applied to alligator weed and beans did not generate ^{14}C- labeled carbon dioxide (Simsiman and Chesters, 1976).

In the water column.--Ultimate biodegradation half-lives, that is biodegradation to CO_2 and water, were calculated during studies that used flasks containing radiolabeled ^{14}C diquat and water and sediment from Lake Mendota, Wisconsin (Simsiman and Chesters, 1976). The resulting aerobic half-life was 31.9 days, and the anaerobic half-life was 49.5 days.

When the microbial degradation rate is coupled with sorption, photolysis, and other minor fate processes, diquat overall aqueous half-lives ranged from 0.8 to 3.8 days (Frank and Comes, 1967; Grzenda and others, 1966; Yeo, 1967; Simsiman and Chesters, 1976) in a variety of environments and laboratory studies.

On particles.--Diquat is strongly bound to sediment particles in such a way that it is not readily biodegradable (Eisler, 1990). Diquat persisted in sediments longer than 160 days in a pond study conducted by Frank and Comes (1967).

Abiotic oxidation/reduction reactions in the water column

Hydrolysis.--Diquat is not significantly subject to hydrolysis in the water column under environmental conditions (Reinert and Rodgers, 1987).

Photolysis.--Photodecomposition of diquat occurs on surfaces and in aqueous solutions (Simsiman and others, 1976). The photolysis half-life of diquat is from 2 to 11 days (table 2). The rate of degradation is related to the intensity of the sunlight to which the diquat is exposed. Slade and Smith (1967) exposed diquat solutions to natural sunlight, which resulted in identical decomposition products; 70 percent of the diquat degraded within 3 weeks. Smith and Grove (1969) proposed two photolysis pathways. The major pathway is diquat to 1,2,3,4-tetrahydro-1-oxopyrido (1,2a) -5-pyrazinium salt, to picolinamide, to picolinic acid, and finally to volatile fragments. The minor pathway produces two pyridone compounds.

Published Studies

Field Studies

Langeland and others (1994) applied diquat and rhodamine WT dye to three 1.6- hectare (4-acre) plots in Orange Lake, Fla., with and without a polymer to aid in sinking and, thereby, limiting the distance they could be transported. Concentrations of diquat and dye were measured at three depths in the water column--just below the water surface, at the midpoint of the water column, and just above the flocculent layer on the bottom. The polymer did not affect the movement of either diquat or dye out of the test plots.The half-life of diquat within all the test plots ranged from 25 to 39 hours. Diquat was not detected in any samples 168 hours after application or more than 61 meters (200 feet) from the edges of the test plots. Dye and diquat concentrations were weakly correlated ($r = 0.42$, $p = 0.001$) during the first 2 hours after application. Dye and diquat concentrations as a function of depth were affected by temperature gradients with depth in the water column. Rhodamine WT cannot be used to predict the concentration of diquat because the dye concentration does not decrease as rapidly as the concentration of diquat. Therefore, rhodamine WT can be used as a conservative indicator of potential diquat transport after application.

Langeland and DeMont (1986) made five operational recommendations to minimize transport of non-persistent aquatic herbicides from treatment areas in lakes or impoundments. (1) Consider local historical weather data, the phenology of the plants targeted for treatment, the schedule of the use of the water body, and the water quality to choose the month of treatment. (2) Use current local weather forecasts to choose the day of application. Apply the herbicide between weather fronts to avoid high winds, runoff, and turbidity. (3) Apply the herbicide near dawn when wind velocity is lowest to minimize wind activity. (4) Treat shallow areas. Shallow littoral areas generally do not have strong currents. (5) Release hypolimnetic water, if possible, to keep the lake level below the level of the spillway.

An extensive study using dye was performed at two North Carolina lakes (impoundments) by Langeland and DeMont (1986) to determine the conditions that influence the transport of herbicides applied to lakes and impoundments. Wind direction has a strong influence on lake currents. If the lake or impoundment is long, narrow, and less than 9 meters (30 feet) deep, currents induced by the wind are along the longitudinal axis of the lake, even when the wind direction is almost perpendicular to the longitudinal axis.

Shorelines also influence lake currents. Currents parallel to the shoreline entrain on-shore flow, so that the on-shore currents never reach the shoreline. On-shore flow creates return flow in the opposite direction, at depth. Eddy currents are created on the windward and leeward sides of promontories or peninsulas and shallow coves or indentations in the shore line. Large coves increase the velocity of return flow generated by on-shore flow.

Numerical Simulations

Corwin and Farmer (1985) developed a mathematical model that estimates the rate of diffusion of a pesticide from bottom sediment into the overlying water column. The finite-difference

model can be used to describe a stream or well-mixed lake or impoundment. The model generates the adsorbed phase vertical concentration distributions in sediment at specified time intervals. Because pesticide half-lives reported in the literature vary widely, the simulation results can be considered accurate within only one order of magnitude. The experimentally determined pesticide half-lives found in the literature depend on the conditions under which the pesticide behavior was studied. More precise simulations are possible if experimentally determined half-lives measured under a specific set of conditions are available.

Corwin and Farmer (1985) characterized the chemical and physical properties of two particle size fractions, which were retained on a 2- and a 0.25-millimeter (0.079- and 0.001-inch) screen, from eight lake, reservoir, and stream-bottom sediment samples obtained from five southern California and three northern California water bodies. Adsorption-kinetic studies were conducted on three of the eight sediments using a 48-hour equilibration time for adsorption. An initial rapid rate of sorption followed by a slow, steady rate indicated that diquat redistributed within the soils. Ninety-five percent of the mass adsorbed over 10 days was desorbed in the first 48 hours. Correlations between the chemical and physical properties of each of the eight sediments and the Langmuir adsorption affinity constant k and Langmuir adsorption maxima b, respectively, indicated that only surface area was highly correlated. No desorption at concentrations equal to or less than 2,500 micrograms per liter was observed; this was attributed to the cation exchange of diquat onto clay particles. A linear relation between the slope (1/b) of the desorption isotherm and the initial diquat concentration was determined.

Petit and others (1995) reviewed the major physical, chemical and microbiological fate processes of three herbicides, including diquat, in riverine systems. The article concentrates on three fate processes that affect diquat in the environment--biodegradation, sorption, and photolysis. Values from the literature for sorption partitioning coefficients, and biodegradation and photolysis half-lives, that can be used in numerical simulations of the fate of diquat are shown in table 2. The authors' recommended strategy is to subdivide the river into short sections or volumes in which fate processes, such as biodegradation, sorption, and photolysis, are numerically simulated in each environmental compartment (air, water column, stream-bottom sediment, and suspended sediment). The masses contained in each environmental compartment are then used as initial masses in the adjacent downstream river section or reach. The recommended modeling strategy is illustrated by a flow chart showing the boundary conditions and the reactions occurring in environmental compartments, such as the water column, stream-bottom sediment, and suspended sediment.

Summary of Environmental-Fate Investigations and Field Studies

Diquat is an organic cation that is soluble in water to 700 grams per liter. It is strongly sorbed to solids, primarily by ionic binding; when sorbed to solids, it is not available to be microbially degraded. Diquat is not significantly affected by the processes of volatilization or hydrolysis. Diquat is not degraded within treated plants, but is slowly degraded by microorganisms aerobically and anaerobically (half-lives of 32 and 50 days, respectively). Diquat undergoes photolysis with resulting half-lives ranging from 2 to 11 days. Turbid water will hinder photolysis, resulting in longer half-lives, but will provide suspended solid surfaces for diquat to sorb to; after the solids settle, the diquat is removed from the water column.

The two environmental process which remove diquat quickly from the water column are photolysis and sorption. Sorption will predominate in turbid water, whereas photolysis will predominate in clear water. The overall water-column half-life obtained from field studies ranged from 0.8 to 3.8 days.

References Cited For Diquat

Birmingham, B.C., and Colman, B., 1983, Potential phytotoxicity of diquat accumulated by aquatic plants and sediments: Water, Air, and Soil Pollution, v. 19, no. 2, p. 123-131.

Budavari, S., O'Neil, M.J., Smith, A., and Heckelman, P.E., 1989, The Merk Index-an encyclopedia of chemicals, drugs, and biologicals (11th ed.): Rahway, N.J., Merk and Company, p. 709.

Crafts, A.S., 1975, Modern Weed Control: Berkeley, Calif., University of California Press, 440 p.

Coats, G.E., Funderburk, H.H., Jr., Lawrence, J.M., and Davis, D.E., 1964, Persistence of diquat and paraquat in pools and ponds: Proceedings of the 17th Southern Weed Control Conference, v. 17, p. 308-320.

Corwin, D.L., and Farmer, W.J., 1985, A mathematical model of diffusion under saturated conditions to assess the pollution potential of herbicides to aquatic systems: Hilgardia, v. 53, no. 3, p. 1-36.

Davies, P.J.T., and Seaman, D.E., 1968, Uptake and translocation of diquat in *Elodea:* Weed Science, v. 16, p. 293-295.

Eisler, R., 1990, Paraquat hazards to fish, wildlife, and invertebrates: a synoptic review: Laurel, Md., Patuxent Wildlife Research Center, Contaminant Hazard Reviews, Biological Report No. 85, 22p.

Faust, S.D., and Hunter, N.E., 1965, Chemical methods for the detection of aquatic herbicides: Journal of the American Water Works Association, v. 57, p. 1028.

Frank, P.A., and Comes, R.D., 1967, Herbicidal residues in pond water and hydrosoil: Weeds, v. 16, p. 210-213.

Funderburk, H.H., Jr., and Lawrence, J.M., 1964, Mode of action and metabolism of diquat and paraquat: Weeds, v. 12, p. 259.

Grzenda, A.R., Nicholson, H.P., and Cox, W.S., 1966, Persistence of four herbicides in pond water: Journal of the American Water Works Association, v. 58, p. 326-332.

Hiltibran, R, C., Underwood, D.L., and Fickle, J.S., 1972, Fate of diquat in the aquatic environment: Urbana, Ill., University of Illinois, Water Resources Center, Research Report 52, 45 p.

References Cited for Diquat--Continued

Khan, S.U., 1974, Adsorption of bipyridylium herbicides by humic acid: Journal of Environmental Quality, v. 3, p. 202-206.

Klingman, G.C., Ashton, F.M., Noordhoff, L.J., 1975, Weed Science: Principles and practice: New York, John Wiley and Sons, 431 p.

Langeland, K.A., and DeMont, D.J., 1986, Considerations for using herbicides for aquatic weed control in domestic water supplies of North Carolina: Raleigh, N.C., Water Resources Institute of the University North Carolina, Report No. 227, 116 p.

Langeland, K.A., Fox, A.M., Laroche, F.B., Martin, B.B., Martin, D.F., Norris, C.D., and Wang, C., 1994, Diquat distribution in water after application to submerged weeds: Water Resources Bulletin, v. 30, no. 1, p. 93-97.

Mees, G.C., 1960, Experiments on the herbicidal action of 1-1'-ethylene-2, 2' -dipyridylium dibromide: Annals of Applied Biology, v. 48, p. 601.

Murphy, K.J., and Barrett, P.R.F., 1990, Chemical control of aquatic weeds, *in* Pieterse, A.H., and Murphy, K.J., eds., Aquatic weeds--The ecology and management of nuisance aquatic vegetation: Oxford University Press, p. 136-173.

Newbold, C., 1975, Herbicides in aquatic systems: Biological Conservation, v. 7, no. 1, p. 97-118.

Petit, V., Cabridenc, R., Swannell, R.P.J., Sokhi, R.S., 1995, Review of strategies for modelling the environmental fate of pesticides discharged into riverine systems: Environment International, v. 21, no. 2, p. 167-176.

Pionke, H.B., and Chesters, G., 1973, Pesticide-sediment-water interactions: Journal of Environmental Quality, v. 2, p. 29-45.

Reinert, K.H., 1989, Environmental behavior of aquatic herbicides in sediments, *in* Reactions and movement of organic chemicals in soils: Proceedings of a symposium of the Soil Science Society of America and the American Society of Agronomy, Atlanta, Ga., November 30 to December 1, 1987, SSSA Special Publication No. 22, p. 335-348.

Reinert, K.H., and Rodgers, J.H., 1987, Fate and persistence of aquatic herbicides: Reviews of Environmental Contamination and Toxicology, v. 98, p. 61-98.

Sewell, W.D., 1970, Diquat residues in two New York lakes: Proceedings of the Northeast Weed Control Conference, v. 24, p. 281-282.

Simsiman, G.V., and Chesters, G., 1976, Persistence of diquat in the aquatic environment: Water Research, v. 10, p. 105-112.

Simsiman, G.V., Daniel, T.C., and Chesters, G., 1976, Diquat and endothal: Their fates in the environment: Residue Reviews, v. 62, p. 131-174.

References Cited for Diquat--Continued

Slade, P., and Smith, A.E., 1967, Photochemical degradation of diquat: Nature, v. 213, p. 919-920.

Smith, A.E., and Grove, J., 1969, Photochemical degradation of diquat in dilute aqueous solution and on silica gel: Journal of Agricultural and Food Chemistry, v. 17, p. 609-613.

Soderquist, C.J., and Crosby, D.G., 1972, The gas chromatographic determination of paraquat in water: Bulletin of Environmental Contamination and Toxicology, v. 8, p. 363.

Stanley, R.A., and Gangstad, E.O., 1987, Technical review of factors affecting diquat for aquatic use, *in* Gangstad, E.O., and Stanley, R.A., eds., Environmental management of water projects: Boca Raton, Fla., CRC Press, Inc., p. 95-107.

Weber, J.B., 1972, Interaction of organic pesticides with particulate matter in aquatic and soil systems, *in* Faust, S.D., ed., Fate of organic pesticides in the aquatic environment, Advances in Chemistry Series 111: Washington, D.C., American Chemical Society, p. 55-120.

Weed Science Society of America, 1983, Herbicide Handbook: Champaign, Ill., Weed Science Society of America, 515 p.

Yeo, R.R., 1967, Dissipation of diquat and paraquat and the effects on aquatic weeds and fish: Weeds, v. 15, p. 42-46.

Yuen, S.H., Bagness, J.E., and Myles, D., 1967, Spectrophotometric determination of diquat and paraquat in aqueous herbicide formulations: Analyst, v. 92, p. 375.

ENDOTHALL

Endothall is a heterocyclic organic acid (7-oxabicyclo-2.2.1-heptane-2,3-dicarboxilic acid) (Simsiman and others, 1976). The empirical formula is $C_8H_{10}O_5$. It is related to cantharidin, a natural toxic compound common to many insects (Mari and others, 1979). Commercial formulations are available in liquid or granular form as sodium, potassium, or mono alkylamine salts; trade names are Aquathol (granular potassium salt), Aquathol K (liquid potassium salt), Hydout (liquid alkylamine salt) (Gangstad, 1987), and Hydrothol (N,N-dimethylalkylamine salt) (Sherry Driber, New Jersey Department of Environmental Protection, written commun., 1997). Amine salts of endothall have the greatest herbicidal activity of the commercially available salts, as well as the greatest toxicity to fish (Klingman and others, 1975).

Application Methods and Mode of Action on Susceptible Plants

Endothall affects various physiological and biochemical plant processes, such as photosynthesis, respiration, and ribonucleic acid synthesis (Murphy and Barrett, 1990). Endothall inhibits protein synthesis (Mann and others, 1965) and retards lipid metabolism (Mann and Pu, 1968). Therefore, the primary mode of herbicidal activity is imperfectly understood (Simsiman and others, 1976).

Endothall acts as a contact herbicide which is translocated easily (Murphy and Barrett, 1990). It is absorbed by the roots and translocated to the tops of plants by the transpiration stream, but is not translocated from the tops of plants to the roots by the phloem (Gangstad, 1987). The main target weeds are submerged species; endothall tends to have a higher efficacy above 18 °C (Celsius) (64.4 °F (Farenheit)). It is particularly effective against weeds which are associated with warm waters, such as *Hydrilla verticillata* (hydrilla). Normal application rates are 0.5 to 2.5 milligrams acid equivalent per liter (Murphy and Barrett, 1990).

Decomposition of a heavy infestation of weeds treated with endothall may reduce oxygen levels in static water. The label instructs that water with heavy infestations should be treated in sections at 5 to 7 day intervals to prevent suffocation of fish (Gangstad, 1987).

Methods of Analysis

Extraction, Concentration, and Removal of Analytical Interferences

Endothall does not lend itself to water-immiscible solvent extraction from water because the high solubility in water and low octanol-water partition coefficient of endothall result in poor recovery in a nonaqueous immiscible solvent. The ionic properties may allow the use of anion-exchange resin and subsequent desorbtion as a means of isolating and concentrating endothall from water (Simsiman and others, 1976). The use of anion-exchange resin as an isolation and concentration technique has not been reported in the literature as of 1995.

The primary method for analysis of water samples that has been reported in recent literature is described in Sikka and Rice (1973); the steps in the method are concentration, derivatization, extraction, concentration, and analysis by gas-liquid chromatography. The water sample is

acidified to pH 1 with hydrochloric acid, then evaporated to 50 milliliters on a hot plate. The extractant, 200 milliliters of glacial acetic acid, is added to the sample which is then concentrated to 5 milliliters by heating to 118 °C (244 °F). The concentrated solution is added to 10 milliliters of acetic acid. Then 100 milligrams each of anhydrous sodium acetate and 2-chloroethylamine-hydrochloride is added to the concentrated sample water and acetic acid mixture and heated to 120 °C (248 °F) for 1 hour. This derivatization of endothall produces endothall-N-2-chloro-ethylimide. The solution is transferred to a separatory funnel, and 50 milliliters of deionized water is added. The imide is extracted into four sequential 20-milliliters portions of pesticide grade chloroform. The chloroform is separated from the water, composited, and evaporated to near dryness. A volume of 0.5 milliliters of methanol is added to preserve the concentrated chloroform extract.

Determination and Identification

The derivatized and cleaned sample extract is analyzed by isothermal gas-liquid chromatography on a glass column packed with 10 percent SP-2100 on a Supelcoport 100/120 mesh support. The chromatography is performed at an isothermal temperature of 200 °C (392 °F). The carrier gas is helium with a flow rate of 37.5 milliliters per minute. The endothall imide is detected by using a nitrogen-phosphorous detector (Reinert and Rogers, 1984) or a microcoulimetric detector in the nitrogen specific mode (Sikka and Rice, 1973).

Endothall extraction recovery from water ranged from 84 to 95 percent and 85 to 90 percent (Reinert and Rogers, 1985; Sikka and Rice, 1973, respectively). Endothall extraction recovery from sediment was 72 percent (Reinert and Rogers, 1986). A minimum detection level of 2 micrograms per liter and 10 micrograms per kilogram in water and sediment, respectively, determined by using sample fortification (spiking) procedures was reported by Reinert and Rogers (1986).

Fate in Aquatic Systems

When endothall enters the water environment, it is subjected to various chemical, microbiologically mediated, and physical environmental-fate processes. These processes interact both simultaneously and sequentially. Some environmental processes are assumed to be in equilibrium, such as partitioning, which implies that they are reversible. Other processes, such as oxidation/reduction, are assumed to be irreversible. The chemical and physical properties, environmental-rate constants, and partition coefficients are shown in table 3.

Partitioning

Volatilization

Endothall is highly soluble in water, does not have a measurable vapor pressure (Weed Science Society of America, 1983), and therefore, does not significantly partition into the vapor phase from aqueous solution. (See table 3.)

Table 3. Physical and chemical characteristics or properties of endothall

[°C, degrees Celsius; <, less than]

Chemical and physical characteristics or properties	Description or value	Reference
Type of organic compound	Oxabicyclo-dicarboxilic acid	Simsiman and others, 1976
Empirical formulae		
Anion	$C_8H_{10}O_5$	Simsiman and others, 1976
Dipotassium salt (Aquathol K)	$C_8H_{10}O_5K_2$	Simsiman and others, 1976
Disodium salt (Aquathol)	$C_8H_{10}O_5Na_2$	Simsiman and others, 1976
Melting point, °C	Decomposes at 90 °C	Simsiman and others, 1976
Solubility in water, milligrams per liter		
Dipotassium salt	1,228,000	Reinert and Rodgers, 1987
Acid	100,000	Reinert and Rodgers, 1987
Henry's law coefficient, atmospheres meter^3/ mole	Very small	Reinert and Rodgers, 1987
Bioconcentration factor, dimensionless	<1 - 1.1	Reinert and Rodgers, 1987
Octanol-water partition coefficient, dimensionless		
Dipotassium salt	1.36	Reinert and Rodgers, 1987
Acid	1.91	Reinert and Rodgers, 1987
Mode of degradation in water		
Photolysis half-life, days	Stable	Reinert and Rodgers, 1987
Hydrolysis half-life, days	Stable	Reinert and Rodgers, 1987
Biodegradation half-life, aerobic, days	4 - 9	Simsiman and Chesters, 1975
	8.35	Reinert and others, 1986
	2 to 3	Gangstad, 1987
Biodegradation half-life, anaerobic, days	Much longer than aerobic degradation	Simsiman and Chesters, 1975
Sorption partition coefficient,(K_d), dimensionless		
Soils	0.41 - 0.9	Simsiman and Chesters, 1975
	0.958	Reinert and Rodgers, 1986
Organic carbon, (K_{oc})	110-138	Reinert and Rodgers, 1987
Dissociation constants, pH units		
pK_{a1}	3.4	Reinert and Rodgers, 1984
pK_{a2}	6.7	Reinert and Rodgers, 1984

Sorption

Endothal is mobile in sediment. The organic-matter content of the soil plays a major role in the sorption of acidic herbicides, such as endothall (Weber, 1972). The partition coefficients for endothall are low (table 3), indicating that endothall does not have a large potential for being stored or sequestered on sediment either from the streambed or suspended in the water column. Therefore, sorption would not be considered a significant environmental-fate process (Reinert and Rogers, 1987).

Degradation

Biologically mediated reactions

Microbial mediated degradation reactions are the dominant aquatic-fate processes that affect endothall removal (Simsiman and others, 1976).

In plants.--Freed and Gauditz (1961) used ^{14}C-labeled endothall to determine that endothall degraded in the aquatic weed *Elodea* and that the radioactivity was incorporated into several parts of the elodea plant. Although many plants completely metabolize endothall, some aquatic weed species may not extensively degrade endothall that is absorbed by the plant (Simsiman and others, 1976).

In water column.--Microbial transformation and degradation are the dominant aquatic-fate processes that affect endothall persistence. Any environmental variable that increases microbial growth also increases the rate of endothall degradation. Investigators using ^{14}C-labeled endothall deduced that microbial rather than chemical degradation was occurring because the following were observed in experiments (1) reduction of soil moisture and temperature decreased endothall degradation; (2) treatment of soils with non-radiocarbon labeled endothall and nutrients, followed by radiocarbon labeled endothall, increased degradation compared with that in soils that were not pretreated; and (3) addition of microbial inhibitors decreased the production of $^{14}CO_2$ (Simsiman and others, 1976).

A study of biotransformation half-life conducted by Reinert and others (1986) by using ^{14}C-labeled endothall in a shake flask resulted in a half-life of 8.35 days. Overall water-column-decay rates are considered to be a good estimate of endothall biotransformation because other fate processes are insignificant (Reinert and Rogers, 1987). A half-life for the dipotassium salt of 7.3 days was calculated by Yeo (1970) from field studies of farm ponds. Reinert and others (1985) observed a half-life of 4.1 days in plastic greenhouse pools containing water, sediment, and *Myriophyllum spicatum* (Eurasian watermilfoil). Holmberg and Lee (1976) calculated a half-life of 4.1 days in a pond treated with the dipotassium salt.

Anoxic conditions could have a significant effect on the persistence of endothall. Simsiman and Chesters (1975) measured only a 28 percent reduction of endothall applied to a lake during 30 days of anoxic conditions brought about by the weed kill. Rapid disappearance of endothall occurred after restoration of oxygenated water in the lake.

On particles.--Sikka and Rice (1973) reported longer half-lives for endothall in sediment than in water, which they attributed to decreased microbial availability of endothall sorbed to sediment. Only 7 percent of the endothall applied was measured in the sediment during experiments performed by Sikka and Rice (1973). Rodgers and others (1984) and Reinert and Rodgers (1986) reported that endothall persistence in sediments was less than 4 days.

Abiotic oxidation/reduction reactions in the water column

Hydrolysis.--Endothall is not significantly subject to hydrolysis in the water column under environmental conditions (Reinert and Rodgers, 1987).

Photolysis.--Endothall is not significantly subject to photolysis in the water column under environmental conditions (Reinert and Rodgers, 1987).

Published Studies

Field Studies

Two large scale field studies were performed to determine the environmental fate and transport of endothall. These studies were conducted at Gatun Lake, Panama, and Pat Mayse Lake, Texas.

Gatun Lake, Panama

In April 1979, a field study was conducted to determine the effects of endothall treatment on hydrilla in the Frijoles Bay area of Gatun Lake, Panama. Endothall treatments with Aquathol K and Hydout, two salts of endothall, at acid equivalent (ae) treatment rates of 27, 34, and 50 kilograms per hectare (24, 30, and 45 pounds per acre, respectively) and a control of no application were assigned randomly to eight plots (Gangstad, 1987).

Aquathol K and Hydout were effective at controlling hydrilla, the target plant in the field study, at the two larger application rates. Aquathol K dehydrated hydrilla within 24 to 72 hours after treatment at all treatment rates. Hydout was much slower than Aquathol K to produce a noticeable effect on hydrilla, and the noticeable effect only occurred at the two larger treatment rates. Hydout treatment produced noticeable effects 14 to 21 days after treatment. The lowest application rate of Hydout resulted in only slight evidence of hydrilla biomass reduction prior to plant regrowth to the water surface (Gangstad, 1987).

No adverse effects on physical, chemical and biological constituents--dissolved oxygen, pH, water temperature, total organic plus ammonia nitrogen, ammonia nitrogen, and total phosphorous--were observed in the lake water column. Short-term changes in phytoplankton community composition and vertical distribution were observed in the treated plots during the 49-day study of effects of endothall on water quality (Gangstad, 1987).

Dispersion of endothall from the treatment plots to a distance 15 meters (49.2 feet) from treatment-plot boundaries was observed during the first 3 days after application for Aquathol K,

but not Hydout (Westerdahl, 1983). Persistence time for both salts of endothall in the water columns of the treatment plots was less than 7 days. Endothall persistence time in sediment was less than 3 days and more than 21 days for Aquathol K and Hydout, respectively. Endothall persistence time in plant tissue was less than 7 days and more than 21 days for Aquathol K and Hydout, respectively (Westerdahl, 1983).

Pat Mayse Lake, Texas

The target species within Pat Mayse Lake, which has 6,000 acres (2,428 hectares) of surface area, was Eurasian watermilfoil. At the time of the study, June 1983, 90 percent of the recreational shoreline, which included seven bathing beaches and three of eight boat ramps, was either inaccessible or unusable due to heavy growth of Eurasian watermilfoil. The area treated with granular Aquathol K (dipotassium salt) covered 93 acres (38 hectares), extended 50 feet (15 meters) from the shoreline, and followed the contour of the shoreline (Gangstad, 1987). The water depth at 50 feet from the shoreline ranged from 6 to 10 feet (1.8 to 3 meters). Granular Aquathol K was applied at a rate of 250 pounds per acre (223 kilograms per hectare) by air boat to achieve a desired concentration of 2.0 milligrams per liter ae of endothall at six recreation areas. Only 1.5 percent of the surface area and 0.43 percent of the volume of the lake were treated (Reinert and others, 1988).

Endothall was not detected in the vicinity of the City of Paris, Texas, drinking-water intake, which is located in Pat Mayse Lake on the shore opposite and 4,400 feet (1,341 meters) away from the nearest treated area, nor in the tissue of bluegill sunfish which were inside cages located within each treatment area (Gangstad, 1987). No fish mortality was observed. The watermilfoil fell to the lake bed within 10 days after treatment, and total control of the watermilfoil was achieved within 16 days after treatment (Reinert and others, 1988).

Two of the six recreation areas, Lamar Point and Pat Mayse Park East, treated with endothall were chosen for in-depth study. Although a nominal dose of 2.0 milligrams per liter was calculated for each treatment site, maximum concentrations of 0.41 and 1.64 milligrams per liter ae were measured in samples from Lamar Point and Pat Mayse Park East, respectively, collected on the day of treatment. These maximum concentrations are average values of three grab samples taken at 0.1 meters (0.33 feet) below the surface and at 0.15 meters (0.5 feet) above the water-sediment interface because concentrations of endothall in the upper and lower water column were not significantly different ($p > 0.05$) when tested with the Mann-Whitney U statistical test (Reinert and others, 1988).

Calculated half-lives based on concentrations measured from day of treatment to 2 days after treatment were 0.23 and 0.1 days for Lamar Point and Pat Mayse Park East, respectively. Rapid removal of endothall was caused by dilution, dispersion, and biotransformation. Only a small percentage of the lake area and volume were treated. Horizontal velocities of water were 113.5 and 10.2 feet per hour (34.6 and 3.1 meters per hour) at Lamar Point and Pat Mayse Park East, respectively, when the Aquathol treatment was conducted at the two locations. The biotransformation half-life shown in table 3 indicates that this process strongly contributed to the rapid disappearance of endothall from the lake water column. A mass balance of endothall indicated that biotransformation accounted for 32 percent of the endothall decrease at Lamar Point and 91

percent at Pat Mayse Park East. Dilution and dispersion accounted for the remaining losses of endothall (Reinert and others, 1988). The higher mass loss due to dilution and dispersion at Lamar Point was caused by water velocity an order of magnitude greater than that at Pat Mayse Park East.

Numerical Simulations

Reinert and Rodgers (1986) used endothall rate constants from the literature to develop confidence intervals and identify sources of variance for the results of two predictive environmental-fate numerical model simulations, which were generated with the Exposure Analysis Modeling System (EXAMS) and the Simplified Lake and Stream Analysis model (SLSA). Both numerical simulations used rate constants which originated from laboratory, experimental pool (bench scale), and field investigations. These rate constants showed that endothall, for practical purposes, undergoes only one environmental-fate process, biotransformation. Both EXAMS and SLSA predicted aqueous compartment (water column) half-lives ranging from 7.3 to 7.8 days in the experimental pools. A water column half-life of 4 days was calculated from the experimental pool data, however. During the Pat Mayse Lake field study, concentrations of endothall were below the detection limits (2.0 micrograms per liter in water; 0.01 milligrams per kilogram in sediment) in water column samples 2 to 3 days after treatment and in lake-bottom-sediment samples, 4 days after treatment. By using the rate constant data from the Pat Mayse Lake field study, EXAMS and SLSA predicted half-lives ranging from 3 to 6 days in the water column. The observed half-lives in the water column of Pat Mayse Lake ranged from 0.1 to 0.23 days. Predicted concentrations of endothall in lake-bottom sediment were similar to the measured concentration.

Reinert and Rodgers (1986) reported that the numerical simulation model biotransformation algorithm used in conjunction with the dispersion/dilution algorithm appears to accurately predict endothall half-lives in the water column within one order of magnitude when the numerical simulation models are sufficiently calibrated and the input variables are accurate. Variation in K_p values changed the predicted sediment concentrations to one order of magnitude greater and less than the observed sediment concentrations.

Reinert and others (1987) compared the effects of two different sources of the dependent variables or input values on the predicted environmental half-life of endothall calculated by EXAMS. The first method of obtaining the input values needed for EXAMS was to use data gathered from the literature; measured field values, specifically reservoir flow data; compartment sizes; and solids data (defined as limited parameterization). The second method was to generate laboratory, experimental-pool, herbicide-specific, and field data that mimicked as precisely as possible the environment in which the environmental fate of endothall was to be predicted (defined as intensive parameterization). Environmental input values for the Lamar Point site were the same for both parameterization methods. The methods used to determine environmental input values are described in Reinert and Rodgers (1986). The two methods of parameterization predicted water-column endothall half-lives that were greater than the observed half-life by multiples of 5 to 9; in other words, the predicted values were within an order of magnitude of the observed values.

Predicted concentrations of endothall in sediment from Pat Mayse Lake were all less than the analytical detection limit (0.01 milligrams per kilogram); however, mean observed concentrations of endothall in sediment from Pat Mayse Lake were as great as 2.3 milligrams per kilogram.

Model predictions of concentrations of endothall in the water column were sensitive to changes in horizontal-dispersion and dilution rates, which are a function of flow. For example, a 50 percent increase in the flow rate at Lamar Point resulted in a 27 percent decrease in concentration, and a 50 percent decrease in the flow rate resulted in a 61 percent increase in concentration. When flow rates were adjusted by plus and minus 50 percent, the predicted endothall half-lives were not appreciably different from previous predictions, however (Reinert and others, 1987).

Summary of Environmental Fate Investigations and Field Studies

Endothall is a heterocyclic organic acid and is applied as a sodium, potassium, or alkylamine salt. The alkylamine salt has the greatest herbicidal activity, as well as the greatest toxicity to fish. Endothall salts are highly soluble in water; the solubility limit for the dipotassium salt is 1.2 grams per liter.

Environmental Fate

Endothall does not significantly volatilize or partition from water to air. It does not degrade by the processes of photolysis or hydrolysis. Sorption is not a major or dominant process by which endothall is removed from the water to suspended particles or bottom sediment. The sorption of endothall is affected by aqueous pH.

Aerobic biodegradation removes endothall from the water column faster than any other environmental process. When undergoing aerobic biodegradation, endothall has a half-life of 2 to 9 days. Anaerobic biodegradation results in a much longer half-life for endothall (longer than 30 days) than does aerobic biodegradation.

Field Studies

Two large-scale field studies--Gatun Lake, Panama, and Pat Mayse Lake, Texas--were reported in the literature. The target plants in the Gatun Lake and Pat Mayse Lake studies were hydrilla and Eurasian watermilfoil, respectively.

During the Gatun Lake study, endothall was detected 15 meters (49 feet) outside the boundaries of the treated plots, after the application of the liquid formulation of the dipotassium salt of endothall, because of dispersion (mixing). When the granular formulation of the alkylamine salt of endothall was used, no endothall was detected 15 meters (49 feet) outside the treatment-plot boundaries. The liquid potassium salt of endothall dehydrated the target plant (hydrilla) within 24 to 72 hours after treatment, whereas the granular alkylamine salt produced a noticeable reduction in plant biomass in 14 to 21 days after treatment. The slower die-off rate for the granular alkylamine salt is attributed to the slower release of the active ingredient into solution. Following application of granular alkylamine salt, no adverse changes were measured in the biological, chemical, and physical constituents of the lake water.

For the Pat Mayse Lake study, 1.5 percent of the surface area and 0.43 percent of the volume of the lake were treated. The treated areas were swimming beaches, boat ramps, and recreational shoreline. The treated area nearest the City of Paris, Texas, drinking-water treatment-

plant intake was 4,400 feet (1,341 meters) away, along the opposite shore. Endothall was not detected in the vicinity of the drinking-water treatment-plant intake nor in the tissue of the caged blue gill sunfish located within each of the six treated areas. The watermilfoil died and fell to the lake bottom within 10 days after treatment.

References Cited for Endothall

Freed, V.H., and Gauditz, I., 1961, The absorbtion and metabolism of radioendothall by fish and aquatic plants: Proceedings of the Northeast Weed Control Conference, v. 15, p. 560.

Gangstad, E.O., 1987, Technical review of the factors affecting endothall for aquatic use, *in* Gangstad, E.O., and Stanley, R.A., eds., Environmental management of water projects: Boca Raton, Fla., CRC Press, Inc., p. 85-94.

Holmberg, D.J., and Lee, G.F., 1976, Effects and persistence of endothall in the aquatic environment: Journal of the Water Pollution Control Federation, v. 48, p. 2738-2746.

Klingman, G.C., Ashton, F.M., Noordhoff, L.J., 1975, Weed Science: Principles and practice: New York, John Wiley and Sons, 431 p.

Mann, J.D., Jordan, L.S., and Day, B.E., 1965, A survey of herbicides for their effect upon protein synthesis: Plant Physiology, v. 40, p. 151.

Mann, J.D., and Pu, M., 1968, Inhibition of lipid synthesis by certain herbicides: Weed Science, v. 16, p. 197.

Mari, F., Bertol, E., Volpato, I., Tosti, M., and Orzales, G., 1979, The detection of cantharidin in biological specimens: Journal of Analytical Toxicology, v. 3, p. 264-265.

Murphy, K.J., and Barrett, P.R.F., 1990, Chemical control of aquatic weeds, *in* Pieterse, A.H., and Murphy, K.J., eds., Aquatic weeds--The ecology and management of nuisance aquatic vegetation: Oxford University Press, p. 136-173.

Reinert, K.H., and Rodgers, J.H., 1984, Influence of sediment types on the sorption of endothall: Bulletin of Environmental Contamination and Toxicology, v. 32, no. 5, p. 557-564.

_____ 1985, Release of endothall from Aquathol granular aquatic herbicide: Water Research, v. 19, no. 6, p. 805-808.

_____ 1986, Validation trials of predictive fate models using an aquatic herbicide (endothall): Environmental Toxicology and Chemistry, v. 5, p. 449-461.

_____ 1987, Fate and persistence of aquatic herbicides: Reviews of Environmental Contamination and Toxicology, v. 98, p. 61-98.

Reinert, K.H., Hinman, M.L., and Rodgers, J.H., 1988, Fate of endothall during the Pat Mayse Lake (Texas) aquatic plant management program: Archives of Environmental Contamination and Toxicology, v. 17, no. 2, p. 195-199.

References Cited for Endothall--Continued

Reinert, K.H., Rodgers, J.H., Hinman, M.L., and Leslie, T.J., 1985, Compartmentalization and persistence of endothall in experimental pools: Ecotoxicology and Environmental Safety, v. 10, p. 86-96.

Reinert, K.H., Rodgers, J.H., Leslie, T.J., and Hinman, M.L., 1986, Static shake-flask biotransformation of endothall: Water Research, v. 20, p. 255-258.

Reinert, K.H., Rocchio, P.M., and Rodgers, J.H., 1987, Parameterization of predictive fate models: A case study: Environmental Toxicology and Chemistry, v. 6, no. 2, p. 99-104.

Rodgers, J.H., Reinert, K.H., Hinman, M.L., Dickson, K.L., and Feminella, J.W., 1984, Water quality monitoring in conjunction with the Pat Mayse Lake aquatic plant management program, *in* U.S. Army Corps of Engineers, Proceedings of the 18th Annual Meeting, Aquatic Plant Control, Research Program, Raleigh, N.C., November 14-17, 1983, Miscellaneous Paper A-84-1, p. 17-24.

Sikka, H.C., and Rice, C.P., 1973, Persistence of endothall in the aquatic environment as determined by gas liquid chromatography: Journal of Agriculture and Food Science, v. 21, no. 5, p. 842-846.

Simsiman, G.V., and Chesters, G., 1975, Persistence of endothall in the aquatic environment: Water, Air, and Soil Pollution, v. 4, p. 399-413.

Simsiman, G.V., Daniel, T.C., and Chesters, G., 1976, Diquat and endothal: Their fates in the environment: Residue Reviews, v. 62, p. 131-174.

Weber, J.B., 1972, Interaction of organic pesticides with particulate matter in aquatic and soil systems, *in* Faust, S.D., ed., Fate of organic pesticides in the aquatic environment, Advances in Chemistry Series 111: Washington, D.C., American Chemical Society, p. 55-120.

Weed Science Society of America, 1983, Herbicide Handbook: Champaign, Ill., Weed Science Society of America, 515 p.

Westerdahl, H.E., 1983, Effects of Hydout and Aquathol K on Hydrilla in Gatun Lake, Panama: Journal of Aquatic Plant Management, v. 21, p. 17-21.

Yeo, R.R., 1970, Dissipation of endothall and effects on aquatic weeds and fish: Weed Science, v. 18, p. 282-284.

FLURIDONE

Fluridone (1-methyl-3-phenyl-5-[3-(trifluoromethyl)phenyl]-4(1H)-pyridinone) is a fluorinated pyridinone-based aquatic herbicide (Waldrep and Taylor, 1976) available in granular, liquid, and controlled-release fiber formulations (Sanders and Theriot, 1979; Van and Steward, 1985).

Application Methods and Mode of Action on Susceptible Plants

Fluridone is used primarily against submerged and floating macrophyte species, such as *Hydrilla verticilla* (hydrilla), *Elodea canadensis,* and *Cabomba caroliniana*, but is also effective against some emergent species, such as the various species of *Typha* and *Sagittaria*. Application rates range from 0.1 to 1.0 milligrams per liter of active ingredient or, on an areal basis, approximately 0.56 kilograms per hectare (0.5 pounds per acre) of active ingredient for emergent weeds (Murphy and Barrett, 1990).

Schmitz and others (1987) report fluridone to be especially effective against hydrilla by controlling regrowth from subterranean tubers which are resistant to most aquatic herbicides. A single fluridone treatment on tubers of hydrilla achieved 80 to 100 percent control within 7 to 11 months after application (Arnold, 1979).

The principal mode of action is the inhibition of carotenoid biosynthesis, which is required to prevent chlorophyll photodestruction (bleaching) (Anderson, 1981; Bartels and Watson, 1978). Fluridone is taken up by the roots of susceptible terrestrial plants and translocated to the shoots with no appreciable metabolism taking place (Berard and others, 1978). Fluridone is absorbed into roots and shoots of pondweed and is translocated to a lesser degree than in terrestrial plants with no detectable metabolism (Marquis and others, 1981).

The weeds die slowly as food reserves in the plant are exhausted and are not replaced; symptoms appear 2 to 4 weeks after treatment. The advantage of this slow die-off rate is that ecosystem side-effects, such as deoxygenation of the water or a sudden change in habitat, are minimized, but a slow die-off rate is a disadvantage if rapid weed removal is needed (Murphy and Barrett, 1990).

Hall and others (1984) demonstrated that the minimum sustained (continuous dosing over 12 weeks) concentration of fluridone needed to give greater than 50 percent die-off of Eurasian watermilfoil was from 10 to 20 micrograms per liter of active ingredient. A greater than 50 percent die-off of hydrilla was achieved under the same experimental conditions at 20 micrograms per liter of active ingredient.

Methods of Analysis

Extraction, Concentration, and Removal of Analytical Interferences

Fluridone is extracted from water samples by using dichloromethane; a 2 normal sodium hydroxide/methanol (1 to 1 by volume) solution is used to extract fluridone from samples of

hydrosoil, a mixture of water and water saturated soil. Methanol is used to extract fluridone from fish, plants, and zooplankton samples. The methanolic and the sodium hydroxide/methanol extracts are cleaned and extracted with dichloromethane; then phosphorus tribromide is used to react with the fluridone in the dichloromethane extract to form a brominated derivative. The dichloromethane extract is then purified by using an activated alumina chromatography column (West, 1978; Banks and Merkle, 1979; West and others, 1979). This extraction procedure is also effective in isolating the 4-hydroxyphenyl metabolite (West and Burger, 1980).

Determination and Identification

The presence of a brominated derivative of residual fluridone in soils and water has been determined by electron capture gas-liquid chromatography. The lower limit of detection in water samples is 0.5 to 1.0 parts per billion and in other matrices, such as hydrosoils or plants, is approximately 10 parts per billion (West, 1978; Banks and Merkle, 1979; West and others, 1979). This analytical procedure is also effective in quantifying the 4-hydroxyphenyl metabolite (West and Burger, 1980).

Underivatized fluridone in dichloromethane extracts from an aqueous matrix can be measured directly by gas-liquid chromatography with a nitrogen detector (Muir and others, 1980; Muir and Grift, 1982). This method of analysis has not been widely used, however.

Analysis of fluridone by reverse phase high performance liquid chromatography (HPLC) with an ultraviolet (UV) absorbance detector at 254 nanometers is faster and more accurate than analysis by gas chromatography with an electron capture detector. HPLC is capable of detecting 1 part per billion fluridone in water extracts, and 5 parts per billion can be detected when analyzing an un extracted water sample. Residues from hydrosoils are detectable at 0.01 parts per million using HPLC (West and Parka, 1981). The use of solid phase extraction cartridges, such as Sep Pak, for the extraction of fluridone increases the efficiency of the reverse phase HPLC technique (West and Day, 1981). HPLC also can be used to detect the fluridone-acid metabolite by derivatization of the metabolite to form a methyl ester, which can be detected at 313 nanometers (West and others, 1983).

Separation of fluridone and fluridone metabolites or degradation products is possible by use of thin layer chromatography performed on silica gel plates. Typical solvent and solvent mixtures used as the chromatographic mobile phase are toluene/ethanol (2:1), chloroform/methanol/water/acetic acid (65:25:4:1), methanol/chloroform (3:1), and toluene/acetonitrile/acetic acid (65:35:1). The spots corresponding to fluridone and fluridone degradation products are detected under UV light (Marquis and others, 1982).

Fate in Aquatic Systems

When fluridone enters the water, it is subjected to various chemical, microbiologically mediated, and physical environmental-fate processes. These processes interact both simultaneously and sequentially. Some environmental processes are assumed to be in equilibrium, such as partitioning, which implies that they are reversible. Other processes, such as oxidation/reduction are assumed to be irreversible. The chemical and physical properties, environmental-rate constants, and partition coefficients are shown in table 4.

Table 4. Physical and chemical properties, partition coefficients, and degradation half-lives of fluridone

[°C, degrees Celsius]

Chemical and physical characteristics or properties	Description or value	Reference
Type of organic compound	Fluorinated pyridinone	Reinert and Rodgers, 1987
Empirical formula	$C_{19}H_{14}F_3NO$	Hamelink and others, 1986
Melting point	154 °C	Waldrep and Taylor, 1976
Solubility in water, milligrams per liter	12	Reinert and Rodgers, 1987
Henry's law coefficient, atmospheres meter^3/ mole	$1.0x10^{-6}$ to $8.5x10^{-5}$	Reinert and Rodgers, 1987
Bioconcentration factor, dimensionless	0.9 - 15.5	Reinert and Rodgers, 1987
Octanol-water partition coefficient, dimensionless	74.1	Reinert and Rodgers, 1987
Mode of degradation in water		
Photolysis half-life, days	1 - 6	Muir and Grift, 1982
Hydrolysis half-life, days	Stable	Reinert and Rodgers, 1987
Biodegradation half-life, aerobic, days	2 - 60	Reinert and Rodgers, 1987
Biodegradation half-life, anaerobic, days	90 - 360	Murphy and Barrett, 1990
Volatilization half-life, days	49.5	Reinert and Rodgers, 1987
Sorption partition coefficient,(K_d), dimensionless	3.26	McCowen and others,1979
Organic carbon, (K_{oc})	883 - 6,761	Reinert and Rodgers, 1987
Dissociation constant, pK_b, pH units	1.7	Mossler and others, 1991

Partitioning

Volatilization

Volatilization is not a major environmental process that alters aqueous concentrations of fluridone. Henry's law coefficients shown in table 4 are approximately 1.0×10^{-6} to 85×10^{-6} atmospheres meter^3/ mole, which results in a half-life of 49.5 days in quiescent bodies of water (Reinert and Rodgers, 1987).

Sorption

Both ionic and hydrophobic interactions with sediment are responsible for the strong sorption of fluridone to soils and sediments (Shea and Weber, 1983). Fluridone is a weak base that ionizes in low pH water to a cation (Weber, 1980a). In aqueous absorption/desorption studies, fluridone was shown to sorb to organic particulate matter and montmorillonite clay minerals. The sorption phenomenon was pH dependent for both organic and inorganic particles; sorption increased (approximately 40 percent increase in sorbed fluridone) as the pH was reduced from 6.2 to 3.5 (Shea and Weber, 1983; Weber, 1980a; 1980b).

The fluridone organic carbon partition coefficient ranged from 883 to 2,462 in a pond study in Canada, and only 3.9 to 18.1 percent of the sorbed fluridone on the pond hydrosoils was desorbed in the laboratory (Muir and others, 1980). Under actual field conditions, however, fluridone probably desorbs gradually from the hydrosoil to the water column (West and others, 1983).

Degradation

Biologically mediated reactions

Biologically mediated degradation reactions are only a minor aquatic-fate process affecting fluridone persistence.

In plants.--The studies conducted by Muir and others (1980) and West and others (1979) indicate that fluridone is not degraded in higher plants that are susceptible to fluridone, because fluridone-treated dead and decaying vegetation released fluridone residues into the hydrosoil.

In water column.--Mossler and others (1991) used two microbial consortia (a mixed culture), each collected from one of two lakes, to degrade fluridone in an aqueous solution. Microorganisms from a lake with no previous application of fluridone and those from a lake with prior fluridone applications degraded 40 and 26 percent of fluridone, respectively, over 150 days with no light exposure. This experiment was repeated with 12-hour light exposures per day and resulted in a 29- and 9-percent loss of fluridone for microorganisms with no previous exposure and previous exposure, respectively, to fluridone in lakes. This result indicated that microorganisms containing chlorophyll do not contribute to the degradation of fluridone. The microbial culture with no previous lake exposure to fluridone was then exposed to fluridone *in vitro* in the laboratory; increased degradation rates for fluridone resulted. The proposed mechanism for the increased degradation rate was enzyme induction. When other carbon sources were added to the mineral plus fluridone solutions little of the fluridone, 4 to 8 percent, was degraded by the microorganisms, indicating that other carbon sources are preferentially mineralized.

The biodegradation process generally removes a minor amount of fluridone from the water column; half-lives of fluridone in non-turbid water are listed in table 4. The half-life resulting from biodegradation is an order of magnitude lower than that from photolysis. In turbid waters or other environmental conditions that significantly reduce the amount of light energy entering the water column, however, biodegradation could be the major process for removing fluridone from the water column.

On particles.--Fluridone degrades slowly in hydrosoil. The anaerobic half-life of fluridone in hydrosoil ranges from 3 to 12 months (table 4). Fluridone also may be strongly bound to particles, montmorillonite (Langeland and DeMont, 1986), or organic matter, so that fluridone is not available to be degraded by microbially mediated reactions (Marquis and others, 1982; Muir and Grift, 1982).

Abiotic oxidation/reduction reactions in the water column

Hydrolysis.--Fluridone is not significantly subject to hydrolysis in the water column under environmental conditions (Reinert and Rodgers, 1987).

Photolysis.--The primary environmental-fate process that affects fluridone concentrations in the water column is photolysis (McCowen and others, 1979; West and others, 1983; Hamelink and others, 1986). A photolysis half-life of 5.8 days (table 4) was observed in flasks containing pond water (Muir and Grift, 1982).

Saunders and Mosier (1983) studied the characteristics that affect the rate of degradation by photolysis by using ^{14}C-fluridone in a laboratory experiment. The only combination that resulted in a statistically significant difference was a pH of 6 and deaerated distilled water, which resulted in the longest half-life. After 88 hours of illumination at 500 microwatts per square centimeter, only 47 percent of the initial radioactivity remained. Volatile degradation products were identified as benzaldehyde, 3-(trifluoromethyl) benzaldehyde, benzoic acid, 3-(trifluoromethyl) benzoic acid, and N-methylformamide. Concentrations of N-methylformamide did not decrease during this study.

Published Studies

Field Studies

Langeland and DeMont (1986) found that fluridone was more persistent than either diquat or endothall. A liquid formulation of fluridone applied to Apex Pond and Whispering Pines Pond, North Carolina, showed an inverse relation between the concentration of fluridone and the elapsed time after application. The elapsed time after application at which the concentration of fluridone was not detected (64 days for Apex Pond and 69 days for Whispering Pines Pond) agreed with the values observed by West and others (1983). Fluridone formulation in granules produced the maximum fluridone concentration in the water column at 17 days after application instead of immediately after application, as was observed for the liquid formulation.

Schmitz and others (1987) applied 2.25 kilograms per hectare (2 pounds per acre) of fluridone in aqueous suspension to 50 percent of a 98.8-hectare (244-acre) lake in Orange County, Florida, primarily to control hydrilla. Fluridone did not affect the submerged vegetation during the fall-winter application from October 1982 to February 1983. As water temperatures increased during the spring, hydrilla biomass declined at an average rate of 0.178 kilograms per square meter per month (0.0364 pounds per square foot per month) during March to August 1983. By summer, 192 days after the last application, the hydrilla could not be found within the lake. The fluridone residues in hydrosoil peaked at 5 percent of the application rate, and the peak occurred within the

March to August period of decline in the aquatic plant biomass. Residue concentrations increased during the next winter following the application of fluridone. Concentrations of fluridone were detected, and vegetation was controlled for a total of 86 weeks from the date of last application.

Fox and others (1991) observed significant correlations, at a correlation coefficient $r > 0.9$, between Rhodamine WT dye and fluridone concentrations in the Three Sisters tidal canals and a shallow lake in the Upper Saint Johns River, Florida, during 340 hours following application. The half-lives of the dye and fluridone (8.7 and 9.1 hours, respectively) were not significantly different over the 340-hour period. Several mechanisms for mixing, such as thermal gradients that changed daily and tidal exchange, were observed in these surface waters.

Leslie and others (1993) studied the fate and transport of an aqueous suspension of fluridone (Sonar AS) after application to Lake Hellen Blazes, Little Lake Sawgrass, and Lake Sawgrass located in the head waters of the Saint Johns River, Florida. Concentrations of fluridone in the water column within the treatment plots peaked at greater than 200 micrograms per liter less than 6 hours after application and were not detected (<1 microgram per liter) 36 to 48 hours after application. Seven days after treatment, fluridone was detected downstream of the treated lakes at concentrations ranging from 11 to 26 micrograms per liter and 1 to 9 micrograms per liter in 1985 and 1987, respectively. Fourteen days after treatment in 1985, 7 micrograms per liter was measured in water samples collected at a drinking-water treatment-plant intake located 8 kilometers (4.8 miles) from treated areas in the upstream lake. The potable water produced at the treatment plant did not contain measurable concentrations of fluridone in 1985. In 1987, 1 to 4 micrograms per liter of fluridone was measured in water samples collected at the drinking-water treatment-plant intake, and the potable water contained 1 to 2 micrograms per liter of fluridone. The area of the lake covered by hydrilla was reduced to 10 to 60 percent of the original area in 1985 after treatment with fluridone, and the reduction lasted 4 to 12 months after treatment. Fluridone was present in water-column samples collected from the river system downstream from the treatment areas for 50 and 28 days in 1985 and 1987, respectively. Greater river flow in 1987 probably accounted for the lower concentrations and shorter persistence times of fluridone, and for the smaller areas of aquatic vegetation die-off.

Numerical Simulations

There were no numerical simulations of the environmental fate and transport of fluridone in the publications reviewed for this report.

Summary of Environmental Fate Investigations and Field Studies

Environmental Fate

Fluridone is a fluorinated pyridinone herbicide available in granular, liquid, and controlled time-release formulations. Fluridone is sparingly soluble in water with a solubility limit of 12 milligrams per liter.

Fluridone does volatilize from the water-column; however, the partition coefficient (Henry's law) is so small (10^{-6}) that volatilization is not a process that will remove fluridone

quickly (estimated half-life, 49.5 days) from the water-column. Fluridone partitions readily from the water column into particulate organic matter because of the high partition coefficient (K_{OC} = 883 to 6,761), then slowly desorbs back into the water column over time.

Fluridone is removed from the water-column by the following degradation processes listed in increasing order of the removal half-life: photolysis (1-6 days), aerobic biodegradation (2-60 days), and anaerobic biodegradation (90-360 days). Photolysis is hindered by suspended matter (turbidity) in the water or by dense plant surface cover. Fluridone does not undergo hydrolysis and is not degraded after being taken up by the plants to which it is applied.

Field Studies

Field studies of the application of fluridone to several lakes and ponds in North Carolina showed that fluridone was more persistent than either diquat or endothall. Fluridone was detected for a longer period after treatment.

In fall 1992, during the field study of a lake in Orange County, Florida, 2.2 kilograms per hectare (2 pounds per acre) of a liquid suspension of fluridone was applied to hydrilla. A complete die-off occurred within 192 days after treatment. Fluridone concentrations were detected 602 days after application.

During a field study of lakes in the head waters of the St. Johns River, Florida, concentrations of fluridone greater than 200 milligrams per liter were observed in the water column less than 6 hours after treatment. No fluridone was detected (< 1 microgram per liter) 36 to 48 hours after treatment. Seven days after treatment, fluridone was detected downstream from the treated lakes. Fourteen days after treatment, 7 micrograms per liter of fluridone was measured at a drinking-water treatment-plant intake 8 kilometers (4.8 miles) downstream from the treated lakes. Fluridone was not measured in the potable water produced by the treatment plant. After a second treatment at the same lake 2 years later, fluridone concentrations ranged from 1 to 4 micrograms per liter in samples collected at the drinking-water treatment-plant intake. After the second treatment, the potable water produced by the treatment plant contained 1 to 2 micrograms per liter.

References Cited for Fluridone

Anderson, L.W.J., 1981, Effect of light on the phytotoxicity of fluridone in American pondweed (*Potamogeton nodosus Poir.*) and sago pondweed (*Potamogeton pectinatus L.*): Weed Science, v. 29, p. 723-728.

Arnold, W.R., 1979, Fluridone-a new aquatic herbicide: Journal of Aquatic Plant Management, v. 17, p. 30-33.

Banks, P.A., and Merkle, M.G., 1979, Soil detection and mobility of fluridone: Weed Science, v. 27, no. 3, p. 309-312.

Bartels, P.G., and Watson, C.W., 1978, Inhibition of carotenoid synthesis by fluridone and norflurazon: Weed Science, v. 26, p. 198-203.

References Cited for Fluridone--Continued

Berard, D.F., Rainey, D.P., and Lin, C.C., 1978, Absorption, translocation, and metabolism of *fluridone* in selected crop species: Weed Science, v. 26, no. 3, p. 252-254.

Fox, A.M., Haller, W.T., and Shilling, D.G., 1991, Correlation of fluridone and dye concentrations in water following concurrent application: Pesticide Science, v. 31, p. 25-36.

Hall, J.F., Westerdahl, H.F., and Stewart, T.J., 1984, Growth response of *Myriophyllum spicatum* and *Hydrilla verticillata* when exposed to continuous, low concentrations of fluridone: U.S. Army Engineer Waterways Experiment Station, Vicksburg, Miss., Technical Report A-84-1, 32 p.

Hamelink, J.L., Buckler, D.R., Mayer, F.L., Palawski, D.U., and Sanders, H.O., 1986, Toxicity of fluridone to aquatic invertebrates and fish: Environmental Toxicology and Chemistry, v. 5, p. 87-94.

Langeland, K.A., and DeMont, D.J., 1986, Considerations for using herbicides for aquatic weed control in domestic water supplies of North Carolina: Water Resources Institute of the University North Carolina, Raleigh, N.C., Report No. 227, 116 p.

Leslie, A.J., Schmitz, D.C., Kipker, R.L., and Girardin, D.L., 1993, Movement of fluridone in the upper Saint Johns River, Florida: Florida Scientist, v. 56, no. 3, p. 168-177.

Marquis, L.Y., Comes, R.D., and Yang, C.P., 1981, Absorption and translocation of fluridone and glyphosate in submerged vascular plants: Weed Science Society of America Journal, v. 29, p. 229-236.

Marquis, L.Y., Comes, R.D., and Yang, C.P., 1982, Degradation of fluridone in submersed soils under controlled laboratory conditions: Pesticide Biochemistry and Physiology, v. 17, p. 68-75.

McCowen, M.C., Young, C.L., Parka, S.J., and Arnold, W.R., 1979, Fluridone, a new herbicide for aquatic plant management: Journal of Aquatic Plant Management, v. 17, p. 27-30.

Mossler, M.A., Shilling, D.G., Albrecht, S.L., and Haller, W.T., 1991, Microbial degradation of fluridone: Journal of Aquatic Plant Management, v. 29, p. 77-80.

Muir, D.C.G., and Grift, N.P., 1982, Fate of fluridone in sediment and water in laboratory and field experiments: Journal of Agricultural Food and Chemistry, v. 30, p. 238-244.

Muir, D.C.G., Grift, N.P., Blouw, A.P., and Lockhart, W.I., 1980, Persistence of fluridone in small ponds: Journal of Environmental Quality, v. 9, no. 1, p. 151-156.

Murphy, K.J., and Barrett, P.R.F., 1990, Chemical control of aquatic weeds, *in* Pieterse, A.H., and Murphy, K.J., eds., Aquatic weeds--The ecology and management of nuisance aquatic vegetation: Oxford University Press, p. 136-173.

References Cited for Fluridone--Continued

Reinert, K.H., and Rodgers, J.H., 1987, Fate and persistence of aquatic herbicides, Reviews of Environmental Contamination and Toxicology, v. 98, p. 61-98.

Sanders, D.R., and Theriot, R.F., 1979, Evaluation of two fluridone formulations for the control of hydrilla in Gatun Lake, Panama Canal Zone: U.S. Army Engineer Waterways Experiment Station, Vicksburg, Miss., Technical Report A-79-3, 29 p.

Saunders, D.G., and Mosier, J.W., 1983, Photolysis of the aquatic herbicide fluridone in aqueous solution: Journal of Agricultural and Food Chemistry, v. 31, p. 237-241.

Schmitz, D.C., Leslie, A.J., Nall, L.E., and Osborne, J.A., 1987, Hydrosoil residues and *Hydrilla verticilla* control in a central Florida lake using fluridone: Pesticide Science, v. 21, p. 73-82.

Shea, P.J., and Weber, J.B., 1983, Fluridone adsorption on mineral clays, organic matter, and modified Norfolk soil: Weed Science, v. 31, p. 528-532.

Van, T.K., and Steward, K.K., 1985, The use of controlled-release fluridone fibers for control of hydrilla (*Hydrilla verticilla*): Weed Science, v. 34, p. 70-76.

Waldrep, T.W., and Taylor, H.M., 1976, 1-methyl-3-phenyl-5-[3-(trifluoromethyl)phenyl]-4(1H)-pyridinone, a new herbicide: Journal of Agricultural Food and Chemistry, v. 24, no. 6, p. 1250-1251.

Weber, J.B., 1980a, Ionization of buthidazole, VEL 3510, tebuthiuron, fluridone, metribuzin, and prometryn: Weed Science, v. 28, p. 467-474.

Weber, J.B., 1980b, Adsorption of buthidazole, VEL 3510, tebuthiuron, fluridone, metribuzin, and prometryn by organic matter, montmorillonite clay, exchange resins, and a sandy loam soil: Weed Science, v. 28, p. 478-483.

West, S.D., 1978, Determination of residue levels of the herbicide fluridone by electron-capture gas chromatography: Journal of Agricultural and Food Chemistry, v. 26, p. 644-646.

West, S.D., and Burger, R.O., 1980, Gas chromatographic determination of fluridone aquatic herbicide and its major metabolite in fish: Journal of the Association of Official Analytical Chemists, v. 63, no. 6, p. 1304-1309.

West, S.D., Burger, R.O., Poole, G.M., and Mowrey, D.H., 1983, Bioconcentration and field dissipation of the aquatic herbicide fluridone and its degradation products in aquatic environments: Journal of Agricultural and Food Chemistry, v. 31, p. 579-585.

West, S.D., and Day, E.W., 1981, Extraction of aquatic herbicide fluridone from water and determination by high pressure liquid chromatography: Journal of the Association of Official Analytical Chemists, v. 64, no. 5, p. 1205-1207.

References Cited for Fluridone--Continued

West, S.D., Day, E.W., and Burger, R.O., 1979, Dissipation of the experimental aquatic herbicide fluridone from lakes and ponds: Journal of Agricultural and Food Chemistry, v. 27, p. 1067-1072.

West, S.D., and Parka, S.J., 1981, Determination of the aquatic herbicide fluridone in water and hydrosoil: effect of application method on dissipation: Journal of Agricultural and Food Chemistry, v. 29, p. 223-226.

GLYPHOSATE

Glyphosate, or N-(Phosphonomethyl)glycine, is a broad-spectrum, nonselective, post emergent herbicide active against a wide range of annual and perennial species (Baird and others, 1971). It is an organophosphorus compound containing a carbon-phosphorous (C-P) bond. The isopropylamine salt of glyphosate is used for aquatic weed control and is registered for use in all types of aquatic systems (Gangstad, 1983). The isopropylamine salt of glyphosate has been used to control many bank side, emergent, and floating leaved plants (Murphy and Barrett, 1990). In general, emergent and floating leaved plants are susceptible to glyphosate, and submerged plants are not (Barrett, 1985). Barrett (1985) has published a list of susceptible plants with the dose rate required for control, which is too lengthy to reproduce in this report.

Application Methods and Mode of Action on Susceptible Plants

Glyphosate is sprayed directly onto exposed foliage, typically at rates of 1.8 to 2.1 kilograms active ingredient per hectare (1.9 pounds per acre). Application techniques include conventional spray nozzles, controlled drop application (using low volumes), and rope wicks. All these methods have been used with some success in the control of aquatic weeds. After application of glyphosate, treated leaves turn yellow and die within a few days and gradually decay. Unsprayed leaves on the same plant may remain green to the end of the growing season, when natural die-off occurs. The primary effects become apparent the following season when little or no regrowth occurs in the treated area. Poor weed control results if glyphosate is applied too early or too late in the growing season, or to dense weed growth (Murphy and Barrett, 1990).

Glyphosate is absorbed into leaves fairly slowly and is particularly susceptible to being washed off the leaf surface within the first few hours after application, resulting in minimal sorption into the leaf (Casely and Coupland, 1985). The washing off of glyphosate from leaf surfaces occurs as a result of rain, a rise in water level, too great a dilution of active ingredient in the sprayed-on solution, and wave action caused by the passage of a boat through recently treated areas.

Glyphosate inhibits the biosynthesis of aromatic amino acids (Rubin and others, 1982). Cells die because of the inability to synthesize essential proteins and phenolic compounds.

One of the effects of glyphosate uptake by plants is the inhibition of the germination of buds on rhizomes. Inhibition of germination of the buds on rhizomes is an important means of controlling many perennial aquatic weeds (Balyan and others, 1981).

Methods of Analysis

Glyphosate and the major metabolite of glyphosate, aminomethylphosphonic acid (AMPA), possess unusual and distinctive physicochemical properties that make analysis in environmental-aqueous and -nonaqueous matrices and detection of concentrations at the part per billion level a challenge. The physical properties of glyphosate are high water solubility and high polarity (table 5). Glyphosate has three polar functional groups--a phosphonic acid, a carboxylic acid, and a secondary amine. AMPA has two polar functional groups--a phosphonic acid and a primary amine.

Table 5. Physical and chemical characteristics or properties of glyphosate

[°C, degrees Celsius; DI, deionized water]

Chemical and physical characteristics or properties	Description or values	Reference
Type of organic compound	Organophosphorus	Petit and others, 1995
Empirical formulae		
Glyphosate	$C_3H_8NO_5P$	Budavari and others,1989
Isopropylamine salt	$C_3H_{17}N_2O_5P$	Budavari and others,1989
Melting point,°C	230 °C	Budavari and others,1989
Solubility in water, milligrams per liter	12,000	Budavari and others,1989
Henry's law coefficient, atmospheres meter^3/ mole	Insignificant	Reinert and Rodgers, 1987
Bioconcentration factor, dimensionless	0.2 - 1.0	Reinert and Rodgers, 1987
Octanol-water partition coefficient, K_{ow}, dimensionless	5.6×10^{-4}	Reinert and Rodgers, 1987
Mode of degradation in water		
Photolysis half-life, days	21 - 28 (DI water)	Lund-Hoie and Friedstad, 1986
Hydrolysis half-life, days	Stable	Petit and others, 1995
Biodegradation half-life, aerobic, days	15 - 70	Reinert and Rodgers, 1987;
	12	Sacher, 1978
Biodegradation half-life, anaerobic, days	28 (similar to aerobic)	Tooby, 1985
Sorption partition coefficient,(K_d), dimensionless		
Kaolinite	66 - 5193 f(pH)	Reinert and Rodgers, 1987
Goethite	102 - 1826 f(pH)	Reinert and Rodgers, 1987

Extraction, Concentration, and Removal of Analytical Interferences

The major problem to be resolved in the analysis of glyphosate and AMPA is the removal of analytical interferences. Glyphosate must be extracted with water from various matrices containing solids and defies extraction or any subsequent cleanup with organic solvents from the water extract. The Monsanto method (Monsanto Chemical Company, 1977) involves long and complicated cleanup steps, but it is the only method to have been successfully applied to a wide variety of matrices, such as most common plant and animal matrices, soil, and water.

A brief description of the Monsanto isolation method for soil and water follows:

1. Sample preparation by pre-extraction with organic solvents

   Mix samples with one or more of the following solvent systems: n-butanol saturated with water; methanol:chloroform (2:1, volume:volume); and methanol:chloroform (1:2, volume:volume). These pre-extracts are discarded, and the original sample is retained for further processing. If the sample is water, filter it; then begin sample cleanup. If the sample is soil, extract the soil with deionized water by mixing in a blender, then filtering the soil-deionized water mixture or spinning it in a centrifuge to remove particulate matter.

2. Sample cleanup

   Sample cleanup by chromatography using a strong anion exchange resin, A-101D
   A column 1.2 centimeter (0.47 inches) inside diameter by 30 centimeters (12 inches) long is filled with A101D resin and plugged at either end with glass wool. The column is equilibrated with 1 molar solution of ammonium bicarbonate, then flushed with deionized water until it is free of ammonium bicarbonate. The diluted sample pre-extract flows through the equilibrated column at 600 to 800 milliliters per hour. The column is then rinsed with deionized water, which is discarded. After the column is rinsed, glyphosate and AMPA are eluted from the column by a 0.5 molar ammonium bicarbonate solution.

   Sample cleanup by charcoal
   Charcoal clean-up is necessary only for soil-sample extracts. Mechanically shake the fraction collected from the anion exchange column with charcoal (Darco G-60), quantitatively filter it, and concentrate it by using a rotary evaporator.

   Sample cleanup by chromatography using a cation exchange resin, AG50W-X8
   A column 1.2 centimeter (0.47 inches) inside diameter by 20 centimeters (7.9 inches) long is filled with 14.5 centimeters of AG50W-X8 (hydrogen form) and plugged at either end with glass wool. This column is washed and equilibrated with deionized water. The sample is pumped through the column, then eluted with deionized water. The chromatographic fractions to be collected are determined (calibrated) by standard solutions of glyphosate and AMPA. Glyphosate elutes first and is followed by AMPA. One molar ammonium bicarbonate solution is added to each chromatographic fraction, which is then evaporated to dryness prior to derivatization.

3. Derivatization

   Derivatization includes two steps, N-trifluoroacetylation and esterification (methyl-ester) of the N-trifluoroacetylated compound. The final products, which are amenable to analysis by gas chromatography, are N-trifluoroacetyl trimethyl ester of glyphosate and N-trifluoroacetyl dimethyl ester of AMPA.

Monsanto Chemical Company (1977) described two methods for derivatization. Both use trifluoroacetic acid and trifluoroacetic anhydride for N-trifluoroacetylation. One of the two methods uses O-methyl -N,N'-dicyclo hexyl pseudo urea, and the other uses diazomethane for esterification to the methyl ester.

Determination and Identification

Methods found in the literature for the determination, identification, and quantification of glyphosate and AMPA in water and soil are listed in table 6. From the information given in table 6, an appropriate method can be chosen.

Fate in Aquatic Systems

When glyphosate enters the water environment, it is subjected to various chemical, microbiologically mediated, and physical environmental-fate processes. These processes interact both simultaneously and sequentially. Some environmental processes are assumed to be in equilibrium, such as partitioning, which implies that they are reversible. Other processes, such as, oxidation/reduction are assumed to be irreversible. The chemical and physical properties, environmental-rate constants, and partition coefficients are shown in table 5.

Partitioning

Volatilization

Glyphosate is highly soluble in water, does not have a measurable vapor pressure (Henry's law coefficient not calculable) (Weed Science Society of America, 1983; Brandt, 1984), and therefore, does not significantly partition into the vapor phase from aqueous solution (table 5).

Sorption

Glyphosate strongly sorbs to soil colloids, hydrosoil, and suspended solids in the water column. The sorption is strongest in soils with the highest partition coefficient for phosphates, the highest organic-matter content, and the lowest pH (Ching and others, 1975). Under laboratory conditions, glyphosate concentrations in soil column leachate were consistently below the detection limit during a 45-day elution test (Brandt, 1983). Because glyphosate is an acid, ionic, not hydrophobic, interactions are expected to account for the strong sorption of glyphosate (Reinert and Rodgers, 1987). (In table 5, K_d is shown for two minerals.)

Degradation

Biologically mediated reactions

Biologically mediated degradation (usually by bacteria) is considered to be the most important environmental-fate process affecting glyphosate persistence in aquatic environments.

Table 6. Methods for analysis of glyphosate and aminomethylphosphonic acid in soil and water

Method of analysis	Derivatization product	Type of detector	Reference
Gas chromatography	Methyl-N-tri-fluoroacetyl ester	Flame photometric	Monsanto Chemical Co.,1977
High performance liquid chromatography	Pre-column derivatization for fluorogenic labeling	Fluorescence	Cochrane and others, 1982
High performance liquid chromatography	Pre-column derivatization for fluorogenic labeling	Fluorescence	Miles and others, 1986
High performance liquid chromatography	Post column derivatization for ninhydrin labeling	Absorbance at 570 nanometers	Thompson and others, 1989
Thin layer chromatography	No derivatization	Spraying with amine specific reagent	Pavoni, 1978
Molecular emission cavity	No derivatization	Not applicable	Ragab and others, 1979
Polarographic for glyphosate only	Derivatization to nitroso compound	Not applicable	Bronstad and Friestad, 1976
Polarographic for glyphosate only	Derivatization to nitroso compound	Not applicable	Friestad and Bronstad, 1982

In plants.--Little detail is found in the literature concerning the metabolism of glyphosate in plants with roots. The difficulties inherent in the analysis of glyphosate and its potential metabolites in a plant-tissue matrix account for the lack of published information on the subject. Glyphosate has been shown to be extensively metabolized by some plants, but remains virtually intact in others (Coupland, 1985).

In water column.--Biodegradation is considered to be the major environmental-fate process affecting glyphosate persistence in aquatic environments (Brandt, 1983; Weed Science Society of America, 1983). The degradation rate is rapid, about the same rate as sucrose, and depends on the level of microbial activity in the aquatic system (Comes and others, 1976; Rueppel and others, 1977; Bowmer, 1982; Bronstad and Friedstad, 1976). Sacher (1978) determined the water-column half-life to be approximately 12 days in a nonflowing experimental pond. The principal metabolite of glyphosate, AMPA, consistently degrades at a slower rate than glyphosate in shake-flask studies (Rueppel and others, 1977; Bronstad and Friedstad, 1985).

On particles.--The rate of degradation of glyphosate varies for different soils and hydrosoils and has been correlated with general microbial activity, which is a function of many soil characteristics. The rate of degradation is similar for hydrosoils and soils with high microbial activity. Degradation occurs without a lag phase and seems to be a co-metabolic process under both aerobic and anaerobic conditions. The most rapid degradation is in water and soil, and water and

hydrosoil mixtures, at the lowest experimental pH tested (pH 4.2). Sphagnum peat bog hydrosoil had the shortest half-life (49 days) under aerobic conditions at pH 4.2 (Tooby, 1985). Rueppel and others (1977) showed that the half-life of AMPA is much longer than that of glyphosate because AMPA is more tightly bound to particles.

Glyphosate is not readily available to be microbiologically degraded when it is adsorbed onto ion exchange sites on solid surfaces. Glyphosate competes with inorganic phosphorous for the ion exchange sites. Therefore, the extent or capacity of adsorption is correlated with the unoccupied phosphorous exchange sites on the particles (Tooby, 1985). An average half-life of 60 days for soils was reported by Brandt (1983).

Hartman and Martin (1984) showed that suspended sediment influences the acute toxicity of glyphosate to the organisms, *Daphnia pulex* and *Lemna minor*. The experiments showed that glyphosate sorbed to particles was unavailable to plants, such as *Lemna minor*; however, sorbed glyphosate was shown to be available to filter feeding organisms, such as *Daphnia pulex,* when ingested and possibly could be toxic to this organism by this route of exposure.

Abiotic oxidation/reduction reactions in the water column

Hydrolysis.--Glyphosate is not significantly subject to hydrolysis in the water column under environmental conditions (Reinert and Rodgers, 1987). Glyphosate does not contain hydrolyzable functional groups in its molecular structure (Weed Science Society of America, 1983).

Photolysis.--Glyphosate is not significantly subject to photolysis in the water column under environmental conditions (Reinert and Rodgers, 1987). Glyphosate does not contain photolyzable functional groups in its molecular structure (Weed Science Society of America, 1983).

A study by Lund-Hoie and Friedstad (1986) indicates that in deionized water glyphosate exposed to ultra-violet light at 254 nanometers photolyzes (13 percent remained after 63 days) to AMPA, whereas AMPA does not photolyze. The half-life of glyphosate exposed to either ultraviolet light or sunlight was from 3 to 4 weeks. Unfiltered lake water reduced the effect of photolysis. The addition of clay loam to static deionized water initially (1 week after treatment) increased the photolysis removal rate of glyphosate, then subsequently decreased the removal rate compared with that of deionized water alone. The addition of clay loam to unfiltered lake water had an effect on degradation rates similar to the effects described above that were caused by the addition of clay loam to deionized water. The biodegradation rate of glyphosate was not statistically significant when compared to the degradation rate caused by photolysis. These experiments indicated that photolysis may be a more important environmental process in the removal of glyphosate from the water column than had been stated in previously published literature.

Published Studies

Field Studies

Tooby (1985) reviewed several field studies and summarized the results as follows. In static water, the removal of glyphosate from the water column was rapid. Following application of Roundup (3.6 kilograms active ingredient per hectare; 3.2 pounds active ingredient per acre) to a water body 30 centimeters (11.8 inches) deep, the maximum water-column concentration was 1.7 milligrams active ingredient per liter after 4 hours. This concentration decreased by 50 percent 12 hours after application. The limit of detection of the glyphosate analysis was reached 8 days after treatment. Within the same time frame, the concentration of glyphosate in hydrosoil followed a similar pattern of decline, with a concentration that was less than one-tenth that of the concentration in the water column. AMPA was detected and measured in the water column 24 hours after treatment, and the maximum concentration, 0.07 milligrams per liter, was reached 4 days after treatment. AMPA was not detected in the hydrosoil. These results do not agree with the slower rates of degradation reported in laboratory studies and may reflect the influence of suspended-sediment adsorption and photolysis in degrading and removing glyphosate from the water column. Other factors, such as water chemistry, also may have influenced the rate of loss of glyphosate from the water column, but this information was not reported.

In a study conducted by Comes and others (1976), Roundup was metered into two flowing canals at an estimated concentration of 150 micrograms per liter of active ingredient each. Samples were collected downstream at 0.3 kilometers, 1.6 kilometers, and the end of the each canal, either 8 or 14.4 kilometers (0.2, 1.0, and either 5 or 8.9 miles); 79 to 91 percent of the glyphosate remained in the canal water at 0.3 kilometers, 70 percent at 1.6 kilometers, and 58 percent at either 8 or 14.4 kilometers. No times of travel or water velocities were stated. It is possible that a significant amount of the glyphosate added to the canal water was sorbed to suspended sediment.

Goldsborough and Beck (1989) studied the dissipation of glyphosate from the water contained in four small forest ponds (0.0012-0.7 hectares; 0.003-1.7 acres) of differing water quality located in boreal forests in Manitoba, Canada. No target plant species was mentioned. Glyphosate was applied to the water surface by aerial spray application at a rate of 0.89 kilograms active ingredient per hectare (0.8 pounds per acre). This application rate resulted in initial average concentrations in the water column ranging from 14 to 59 micrograms per liter. Glyphosate dissipated rapidly from all ponds; first-order half-lives ranged from 1.5 to 3.5 days. At 38 days, no glyphosate was detected in any of the ponds. The slowest glyphosate dissipation rate and the highest concentrations of calcium and magnesium in both the water and bottom sediments occurred in the pond with the highest pH. AMPA concentrations in all water-column samples were less than or equal to 2.2 micrograms per liter. The maximum AMPA concentration in one pond was measured in water samples collected 30 minutes after treatment. AMPA was not detected in samples from any of the four ponds 11 days after treatment. This result indicated a low rate of biodegradation of AMPA; it also indicated that the primary environmental-fate process was sorption.

Goldsborough and Brown (1993) treated the surface water of three small ponds in the coniferous forests of southern Manitoba, Canada, with an aerial application of 2.1 kilograms per hectare (1.9 pounds per acre) of glyphosate. No target plant species was mentioned. Foliage

samples from plants bordering the ponds were collected immediately after treatment. Pond water and sediment were collected over a period of 265 days after treatment. Samples were analyzed for glyphosate and AMPA. The glyphosate dissipation half-lives ranged from 3.5 to 11.2 days, which is much more rapid than would be expected from biodegradation alone. (See table 5.) AMPA was detected in water-column samples during the first 14 days after treatment, which may indicate that biodegradation or possibly photolysis occurred in the water column. The speculation that photolysis occurred in the water column is based on the Lund-Hoie and Friedstad (1986) experiments to determine the occurrence of photolysis. A mass balance indicated that all the applied glyphosate was not present in the water column. Concentrations of glyphosate and AMPA continued to increase in the sediment samples until day 36 after treatment. Goldsborough and Brown (1993) concluded that sorption to sediment was a major environmental process in the dissipation of glyphosate from the water column. The rate of dissipation was found to be nonlinear, with an initial higher rate followed by a lower rate. The authors hypothesized that two competing environmental processes--biodegradation and sorption--were the cause of the nonlinear rate of dissipation with sorption the cause of the initially higher rate. An alternate hypothesis based on a study by Lund-Hoie and Friedstad (1986) is that the initially higher rate could be caused by photolysis. Lund-Hoie and Friedstad (1986) found that photolysis is a significant environmental process and that photolysis would result in the production of AMPA in the water column. Water alkalinity was determined to be proportional to the half-life of glyphosate when two data sets for water bodies containing different alkalinities were compared. This observation is supported by laboratory experiments that show sorption partition coefficients to be a function of pH (Reinert and Rodgers, 1987). (See table 5.)

Newton and others (1984) studied the fate of glyphosate aerially sprayed at a rate of 3.3 kilograms per hectare (2.9 pounds per acre) on two Oregon forest brush-field ecosystems in the Oregon Coastal Range. Each ecosystem contained a perennial stream. At one site where the spray pattern crossed the stream, concentrations of glyphosate in the stream water were highly variable. Maximum concentrations of sprayed glyphosate at the sampling location occurred when the helicopter passed close to the sample collection point, near the downstream end of the study area. The helicopter then continued spraying upstream. The maximum concentration of 0.27 milligrams per liter was present in samples collected within 20 minutes of the start of spraying. Later, concentrations were lower and varied less with elapsed time. This pattern reflects the effects of mixing due to turbulence and diffusion or residence time. The maximum concentrations of glyphosate (0.55 milligrams per liter) and AMPA (0.14 milligrams per liter) in the stream occurred 14 days after treatment, and the maximum concentration of AMPA was approximately 25 percent that of glyphosate.

Feng and others (1990) monitored glyphosate and AMPA concentrations in a 45-hectare (111-acre) coastal watershed in British Columbia after the application of Roundup at a rate of 2.0 kilograms per hectare (1.8 pounds per acre) of glyphosate. Large concentrations (maximum value of 162 micrograms per liter) were present in samples from a stream that was intentionally sprayed with glyphosate. Large concentrations of glyphosate (maximum value of 110 micrograms per liter) also were present in a sample collected from the same stream during the first rainfall, which occurred 27 hours after treatment. Some streams in the watershed had a no-treatment buffer zone, 10 meters (33 feet) wide along the stream bank. Samples from these streams contained concentrations of glyphosate (maximum value of 2.4 micrograms per liter) that were two orders of

magnitude less than those from the stream that was sprayed directly. After the first rainfall, the concentrations of glyphosate (maximum value of 3.2 micrograms per liter) in the stream that had a no-treatment buffer zone were again two orders of magnitude less than the stream that was sprayed directly.

Numerical Simulations

Petit and others (1995) reviewed the major physical, chemical, and microbiological fate processes of three herbicides; one of the three herbicides is glyphosate. The article concentrates on three fate processes affecting glyphosate in the environment--biodegradation, sorption, and photolysis. Values obtained from the literature for sorption partitioning coefficients, and biodegradation and photolysis half-lives, that can be used in numerical simulations of the fate of glyphosate are shown in table 5. The authors' recommended strategy is to subdivide the river into short sections or volumes in which fate processes, such as biodegradation, sorption, and photolysis, are numerically simulated in each environmental compartment (air, water column, stream-bottom sediment, and suspended sediment). The masses contained in each environmental compartment are then used as initial masses in the adjacent downstream river section or reach. The recommended modeling strategy is illustrated by a flow chart that shows the boundary conditions and the reactions occurring in the water column, stream-bottom sediment, and suspended-sediment environmental compartments.

Zaranyika and Nyandoro (1993) were able to numerically simulate the degradation of glyphosate by using the Michaelis-Menten kinetic model (a first order rate model). The model was simplified to consist of the sum of two degradation reactions. The first reaction involves glyphosate that is bound to microbial organisms. The second reaction involves the glyphosate first sorbed to suspended particles, then bound to microorganisms. The authors recommended that the two rate constants for each aquatic system or compartment of an aquatic system be numerically simulated. In addition, the authors hypothesized that the two rate constants are a function of the water temperature and the pH of both water and stream-bottom sediment because temperature and pH affect microbial activity.

Summary of Environmental Fate Investigations and Field Studies

Environmental Fate

Glyphosate does not volatilize significantly from the water column into air, and volatilization is not a significant process for the removal of glyphosate from the water column. Glyphosate is ionic (an organic acid) and sorbtion is controlled by ion exchange, not hydrophobic interactions. Glyphosate is strongly sorbed to soils or suspended particles with high affinities for phosphates and low pH (<5).

Glyphosate is degraded by some plants, but not others. Microbiologically mediated degradation is the environmental process that removes glyphosate from the water column. The microbial degradation rate is a function of the microbial communities or consortium present and pH. A pH of 4.2 results in the highest degradation rate with a half-life of 12 days. The principal degradation

metabolite AMPA degrades slower than glyphosate. Glyphosate that is ionically bound to particles is not readily available to be microbially degraded and results in a half-life of 60 days in soils.

Glyphosate does not undergo hydrolysis to a significant extent under typical environmental conditions. Although early research indicated that glyphosate would not undergo photolysis, research published in 1986 indicates that photolysis may degrade glyphosate at a rate similar to that of microbial degradation (half-life of 21 to 28 days).

Field Studies

At least six different field studies of the persistence of glyphosate when used as an aquatic herbicide were reviewed. The consensus of the field studies was that the water column half-life was variable within a range of 0.5 to 11 days. This range is smaller than would be expected on the basis of laboratory determined half-lives (12 to 70 days) for microbially mediated degradation. (See table 5.) Perhaps, the environmental processes of dispersion, sorption, and, possibly, photolysis could be the causes of the increased removal rate from the water column. Water quality also was shown to influence the water column half-life of glyphosate. Alkalinity was observed by Goldsborough and Brown (1993) to be proportional to the water column half-life; this relation is supported by laboratory experiments that show that sorption partitioning coefficients are a function of water pH (Reinert and Rogers, 1987) (table5).

References Cited for Glyphosate

Baird, D.D., Upchurch, R.P., Homesly, W.B., and Franz, J.E., 1971, Introduction of a new broad-spectrum post emergent herbicide class with utility for herbaceous perennial weed control: Proceedings of the North Central Weed Control Conference, v. 26, p. 64-68.

Balyan, R.S., Bhan, V.M., Kamboj, R.K., and Singh, S.P., 1981, Translocation of foliage-applied glyphosate into the rhizomes of cattail: Proceedings of the 8th Asian-Pacific Weed Science Society Conference, p. 341-345.

Barrett, P.R.F., 1985, Efficacy of glyphosate in the control of aquatic weeds, *in* Grossbard, E., and Atkinson, D., eds., The Herbicide Glyphosate: London, Butterworths, p. 365-374.

Bowmer, K.H., 1982, Residues of glyphosate in irrigation water: Pesticide Science, v. 33, p. 623-638.

Brandt, E.J., 1983, Rodeo herbicide: toxicological and environmental properties: St. Louis, Mo., Monsanto Chemical Company, Bulletin Number 1, 4 p.

_____ 1984, A health and environmental report on Rodeo herbicide: St. Louis, Mo., Monsanto Chemical Company, Bulletin number 2, 3 p.

Bronstad, J.O., and Friedstad, H.O., 1976, Method for the determination of glyphosate residues in natural waters based on polarography of the N-nitroso derivative: Analyst, v. 101, p. 820-824.

References Cited for Glyphosate--Continued

Bronstad, J.O., and Friedstad, H.O., 1985, Behavior of glyphosate in the aquatic environment, *in* Grossbard, E., and Atkinson, D., eds., The Herbicide Glyphosate: London, Butterworths, p. 200-205.

Budavari, S., O'Neil, M.J., Smith, A., and Heckelman, P.E., 1989, The Merck Index-an encyclopedia of chemicals, drugs, and biologicals (11th ed.): Rahway, N.J., Merck and Company, p. 709.

Casely, J.C., and Coupland, D., 1985, Environmental and plant factors affecting glyphosate uptake, movement, and activity, *in* Grossbard, E., and Atkinson, D., eds., The Herbicide Glyphosate: London, Butterworths, p. 92-123.

Ching, S., Nomura, N., Yauger, W., Uyehara, G., and Hilton, H.W., 1975, Metabolism of glyphosate in Hawaiian sugarcane soils, *in* 1975 Annual Report, Experimental Station of the Hawaiian Sugar Planters' Association: Honolulu, Hawaiian Sugar Planters' Association, p. 39.

Cochrane, W.P., Cohen, H., Greenhalg, R., and Lanquette, M., 1982, The determination of glyphosate in water by high pressure liquid chromatography after florigenic labelling by 7-chloro-4-nitrobenzo-2-oxa-1, 3-diazol: Abstracts of the 5th International Congress of Pesticide Chemistry (IUPAC), v. 7, p. C-11.

Comes, R.D., Bruns, V.F., and Kelly, A.D., 1976, Residues and persistence of glyphosate in irrigation water: Weed Science, v. 24, p. 47-50.

Coupland, D., 1985, Metabolism of glyphosate in plants, *in* Grossbard, E., and Atkinson, D., eds., The Herbicide Glyphosate: London, Butterworths, p. 25-34.

Feng, C.J., Thompson, D.G., and Reynolds, P.E., 1990, Fate of glyphosate in a Canadian forest watershed, 1. Aquatic residues and off-target deposit assessment: Journal of Agricultural and Food Chemistry, v. 38, p. 1110-1118.

Friedstad, H.O., and Bronstad, J.O., 1982, Improved polarographic method for determination of glyphosate herbicide in crop, soil, and water samples: Abstracts of the 5th International Congress of Pesticide Chemistry (IUPAC), v. 7, p. C-12.

Gangstad, E.O., 1983, Herbicidal, environmental, and health effects of glyphosate: Washington, D.C., Office, Chief of Engineers, U.S. Army Corps of Engineers, OCE-NRM-24, 25 p.

Goldsborough, L.G., and Beck, A.E., 1989, Rapid dissipation of glyphosate in small forest ponds: Archives of Environmental Contamination and Toxicology, v. 18, p. 537-544.

Goldsborough, L.G., and Brown, D.J., 1993, Dissipation of glyphosate and aminomethyl-phosphonic acid in water and sediments of boreal forest ponds: Environmental Toxicology and Chemistry, v. 12, p. 1139-1147.

References Cited for Glyphosate--Continued

Hartman, A., and Martin, D.B., 1984, Effect of suspended sediment on the acute toxicity of glyphosate to *Daphnia pulex* and *Lemna minor*: Bulletin of Environmental Contamination and Toxicology, v. 33, p. 355-361.

Lund-Hoie, K., and Friedstad, H.O., 1986, Photodegradation of the herbicide glyphosate in water: Bulletin of Environmental Contamination and Toxicology, v. 36, p. 723-729.

Miles, C.J., Wallace, L.R., and Moye, H.A., 1986, Determination of glyphosate herbicide and (aminomethyl) phosphonic acid in natural waters by liquid chromatography using pre-column fluorgenic labeling with 9-fluorenylmethyl chloroformate: Association of Official Analytical Chemists Journal, v. 69, p. 458-461.

Monsanto Chemical Company, 1977, Pesticide Analytical Manual, Volume 2: Washington, D.C., Food and Drug Administration, Pesticide Registration Section 180.364.

Murphy, K.J., and Barrett, P.R.F., 1990, Chemical control of aquatic weeds, *in* Pieterse, A.H., and Murphy, K.J., eds., Aquatic weeds--The ecology and management of nuisance aquatic vegetation: Oxford University Press, p. 136-173.

Newton, M., Howard, K.M., Kelpsas, B.R., Danhaus, R., Lottman, C.M., and Dubelman, S., 1984, Fate of glyphosate in an Oregon forest ecosystem: Journal of Agriculture and Food Chemistry, v. 32, p. 1144-1151.

Pavoni, G., 1978, Ricerca di glifosate e del sno metabolita principale, l'acido aminometilfosfonico per TLC (Investigation of glyphosate and its principal metabolite, aminomethyl phosphonic acid, by TLC): Bolletino dei chimici dell' Unione Italliana dei Laboratori Provinciali, v. 9, p. 157-161.

Petit, V., Cabridenc, R., Swannell, R.P.J., Sokhi, R.S., 1995, Review of strategies for modelling the environmental fate of pesticides discharged into riverine systems: Environment International, v. 21, no. 2, p. 167-176.

Ragab, M.T.H., Stiles, D.A., and Yeo, J., 1979, The rapid analysis glyphosate and its major metabolite in water by molecular emission cavity analysis: Abstracts of the 1979 Meeting of the Weed Science Society of America, p. 123.

Reinert, K.H., and Rodgers, J.H., 1987, Fate and persistence of aquatic herbicides: Reviews of Environmental Contamination and Toxicology, v. 98, p. 61-98.

Rubin, J.L., Gaines, C.G., and Jensen, R.A., 1982, Enzymological basis for the herbicidal action of glyphosate: Plant Physiology, v. 70, p. 833-839.

Rueppel, M.L., Brightwell, B.B., Schaefer, J., and Marvel, J.T., 1977, The metabolism and degradation of N-phosphonomethylglycine in soil and water: Journal of Agricultural and Food Chemistry, v. 25, p. 517-528.

References Cited for Glyphosate--Continued

Sacher, R.M., 1978, Safety of roundup in aquatic environment: Proceedings of the European Weed Research Society, 5th Symposium on Aquatic Weeds, v. 5, p. 315-322.

Thompson, D.G., Cowell, J.E., Staznik, B., and MacDonald, L.M., 1989, Liquid chromatographic method for quantification of glyphosate and metabolite residues in organic and mineral soils, stream sediments, and hardwood foliage: Association of Official Analytical Chemists Journal, v. 72, p. 355-360.

Tooby, T.E., 1985, Fate and biological consequences of glyphosate in the aquatic environment, *in* Grossbard, E., and Atkinson, D., eds., The Herbicide Glyphosate: London, Butterworths, p. 206-220.

Weed Science Society of America, 1983, Herbicide Handbook: Champaign, Ill., Weed Science Society of America, 515 p.

Zaranyika, M.F., and Nyandoro, M.G., 1993, Degradation of glyphosate in the aquatic environment: An enzymatic kinetic model that takes into account microbial degradation of both free and colloidal (or sediment) particle adsorbed glyphosate: Journal of Agricultural and Food Chemistry, v. 41, p. 838-842.