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SOUTH FLORIDA WATER MANAGEMENT DISTRICT

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HERBICIDE MONITORING PROGRAM FOR THE ACTIVE INGREDIENT GLYPHOSATE

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February 1988

Richard J. Pfeuffer

Water Quality Division
Resource Planning Department
South Florida Water Management District

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EXECUTIVE SUMMARY

The South Florida Water Management District (the District) applies a significant amount of herbicides throughout the District as part of an established right of way, ditchbank, and aquatic weed management program. The herbicides used have been field studied at a variety of locations throughout the nation and are registered by the Environmental Protection Agency and the Florida Department of Agriculture and Consumer Services for the appropriate site and vegetation. However, due to the general concern about herbicide use and possible adverse health and/or ecological effects, an investigation into a south Florida field application was undertaken. This investigation was designed to determine how quickly the active ingredient in a District applied herbicide would dissipate in a south Florida environment. A literature review was conducted to determine which active ingredient should be studied. After consideration for: a) the quantity applied in 1984, b) degradation anomalies, c) toxicity, and d) analytical methodology, it was determined that glyphosate would be the most suitable compound to monitor. In conjunction with the herbicide field monitoring, the Microtox™ Toxicity Analyzer System was employed to determine the relative toxicity of the water samples.

Glyphosate was sprayed on duckweed on the Taylor Creek/L-63N Borrow Canal using the maximum rate of 6 pints per acre or 4.05 pounds of active ingredient per acre (4.54 kg/ha). Surface water and sediment samples were taken the day before spraying, 18 hours later, one week later, and two weeks later. All the glyphosate results for the water and sediment samples were below the minimum detection limit (MDL) of 20 and 40 ppb, respectively. The Microtox™ System ascertained that the samples were not toxic.

The use of glyphosate in this canal system does not appear to present any environmental or health problems as the dissipation rate is very rapid. Since the samples taken before spraying contained no detectable residues, a previous contamination problem does not exist in the study area due to past use.

This is the first in a series of District applied herbicide monitoring studies. Monitoring in 1987 included the compounds fluridone and diquat, as applied in Lake Okeechobee.

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LIST OF ABBREVIATIONS

The following is a list of terms and abbreviations used in the text:

^{0}C: degree centigrade
ha: hectare or hectares, one hectare equals 2.47 acres.
kg: kilogram or kilograms, 1 X 10^3 grams
kg/ha: kilogram per hectare
LC_{50}: abbreviation denoting median lethal concentration, rather than median lethal dose as in the case of LD_{50}.
LD_{50}: abbreviation of median lethal dose, MLD. It indicates the amount of toxicant necessary to effect a 50% kill of the pest being tested. It is expressed in weight of the chemical per unit of body weight (mg/kg). LD_{50} is used to measure the acute oral and dermal toxicity of a chemical. The lower the LD_{50}, the more poisonous the chemical
l: liter
mg: milligram or milligrams, 1 X 10^{-3} grams
mg/l: milligrams per literr
mls: milliliter or milliliters, 1 X 10^{-3} liter
mm: millimeter or millimeters, 1 X 10^{-2} meter
N: normal, or concentrations of solutions are adjusted, or normalized, to account for differences in reacting ratios in chemical reactions. A 1N (1 normal) solution contains one equivalent per liter, or one milliequivalent per milliliter.
nm: nanometer or nanometers, 1 X 10^{-9} meter
%: per cent
ppb: parts per billion, i.e. µg/l or µg/kg
ppm: parts per million, i.e. mg/l or mg/kg
TL_{50}: abbreviation denoting median tolerance level. It indicates the amount of toxicant tolerated by 50% of the organism being tested.
TM: Trade Mark
µg: microgram, 1 X 10^{-6} grams
µg/l: micrograms per liter
µl: microliter or microliters, 1 X 10^{-6} liter

ACKNOWLEDGEMENTS

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ABSTRACT

The herbicide active ingredient glyphosate was monitored in the Taylor Creek/L-63N Borrow Canal system to determine any dissipation anomalies specific to south Florida which may not be included in the product registration or in the technical literature. All the glyphosate sample results were below the minimum detection limit, suggesting that the use of glyphosate in this canal system does not appear to present any environmental or health problems as the dissipation rate is very rapid. Since the pre-application samples were negative, a previous contamination problem does not exist in the study area due to past use.

Key Words:

pesticide, herbicide, glyphosate, residue

INTRODUCTION

The South Florida Water Management District (Figure 1) applies a significant amount of aquatic and terrestrial herbicides over a wide area as part of an established weed management program. The District presently covers an area of 17,930 square miles from Orlando to the Keys and includes all or part of 16 counties. Within this area is a complex interconnected system of canals, levees, lakes, water storage areas, pump stations, and water control structures designed to provide a sufficient quantity and quality of water for all the diverse interests in south Florida. The District has over 1400 miles of canals, 1337 square miles of water conservation areas, and about 20 lakes, the largest of which is Lake Okeechobee (750 square miles). The basic concept of the District's aquatic weed control program is "to control, to the highest degree possible, all exotic nuisance vegetation, while maintaining native vegetation in its most natural balance, to that degree which is compatible with the primary functions of the facility at a given time" (Baker, 1981). In 1984, over one hundred thousand pounds of herbicide active ingredients were applied to achieve this goal. Fourteen different active ingredients or formulations were utilized (Table 1).

The aquatic weed control program is conducted in a manner that will give the most effective and efficient results with the least possible damage to the aquatic environment. However, the presence of a herbicide in the water or sediment provides a possible route for direct human exposure via consumption of water and fish or indirectly via consumption of irrigated crops or animal food products from livestock exposed to the water. These possible impacts of bioaccumulation and toxicity to humans and the aquatic flora and fauna, need to be considered. The general concern about using aquatic herbicides is based on the possible adverse health and/or ecological effects. Consequently, the rate and mode of the herbicide's dissipation is important for determining the impact these compounds may have. The extent of dissipation will depend on a number of factors, including channel dimensions and hydrology, the dosage of the compound, dilution by tributary inflow, dispersion during movement downstream, and loss of herbicide from the water by, for example, uptake into plants and adsorption on to particulate matter and sediments, or bio-degradation or photo-degradation. For these reasons, this program was established to ascertain which herbicides used by the District need to be investigated in order to determine dissipation anomalies specific to south Florida which may not be included in product registration, and to monitor an application event of a suspect herbicide so as to determine its environmental fate in south Florida.

The determination of the most suitable compound to monitor is based on: a) the quantity applied in 1984, b) degradation anomalies, c) toxicity, and d) analytical methodology. Unusual dissipation properties, coupled with the possibility of being unusually toxic to aquatic organisms and the quantity applied, would make an active ingredient a candidate for monitoring.

For this initial study, only the herbicides registered for use on aquatic weeds will be investigated since the majority of the weed control is within the District's waterways. Therefore, Velpar™ and Arsenal™, both terrestrial herbicides, were not considered. Additionally, Cutrine-plus™ will not be considered in this review since its active ingredient, copper, is not an organic compound and cannot be readily discerned in the area of application.

This program also provided the opportunity to utilize the Microtox™ Toxicity Analyzer System to evaluate the relative toxicity of herbicide treated water column samples. The Microtox™ System uses a marine luminescent bacteria as a bioassay test organism. This bioassay is based on the production of light per unit time by living luminescent bacteria, which is a reflection of the rate at which a complex set of energy-producing reactions is operating. The effect of potential inhibitors on light production is measured under defined conditions with the results being analogous to traditional fish and invertebrate bioassays.

Appendix A provides a summary of the herbicide residue and field data. Appendix B provides the details of the information utilized to select the herbicide for monitoring.

SELECTION OF COMPOUND TO MONITOR

Details of the information for compound selection are reported in Appendix B. From the literature review, glyphosate appears to have a longer residence time in the water column and as long a half-life in the sediment as diquat. The remainder of the herbicide active ingredients did not exhibit longer half-lives. Although glyphosate is not as acutely toxic as diquat, the chronic toxicities are similar and lower than the other listed active ingredients. Since slightly more glyphosate than diquat was applied in 1984 (Table B-1, Appendix B), and during this program a suitable analytical methodology for diquat was not available, glyphosate is the compound used by the District best suited for the investigation of its dissipation.

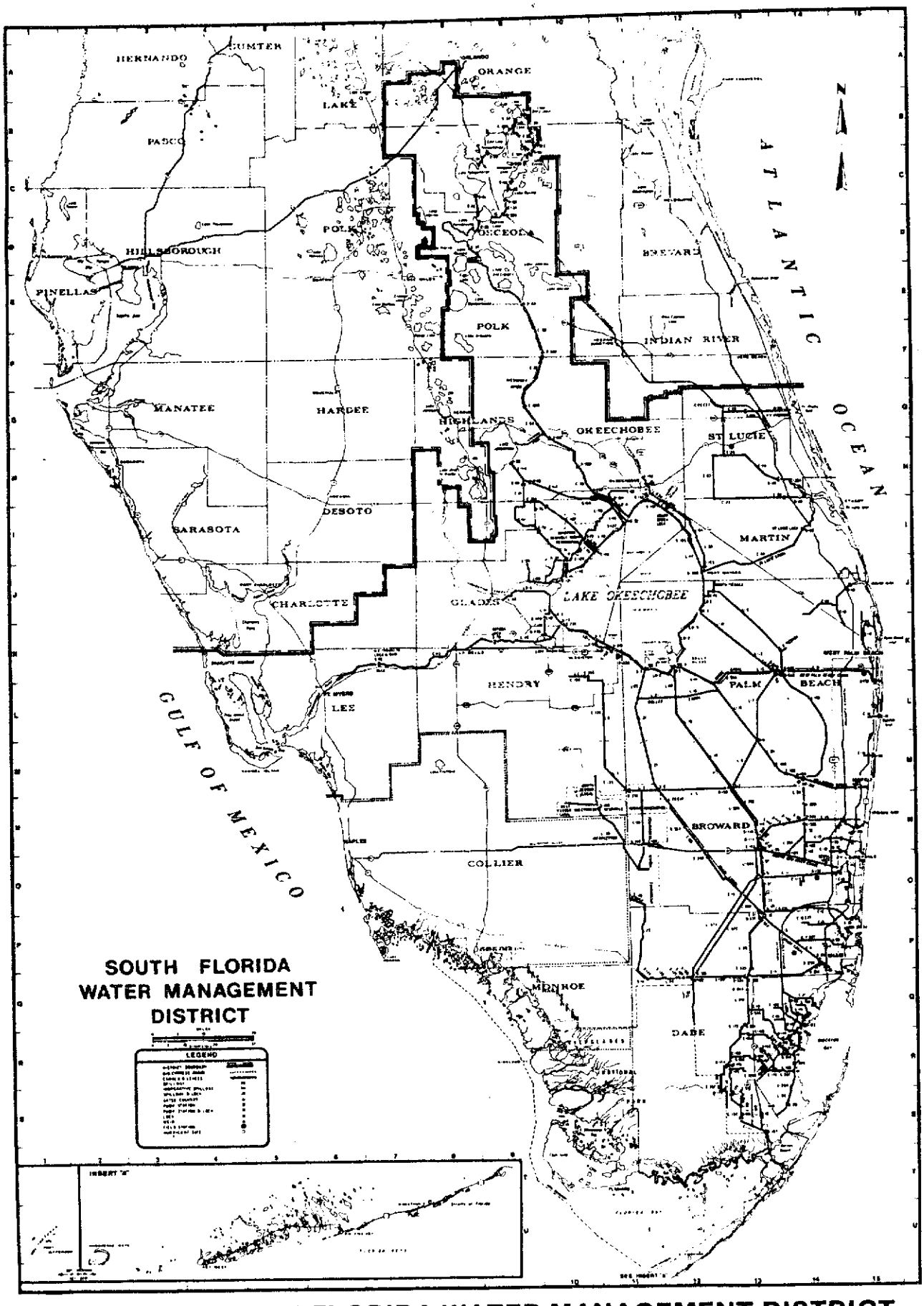

Figure 1 **SOUTH FLORIDA WATER MANAGEMENT DISTRICT**

TABLE 1. HERBICIDES USED BY THE AQUATIC WEED MANAGEMENT PROGRAM

Aquatic Applications	Active Ingredient(s)	% of Active Ingredient	Use[1]
Aquathol K™			
Liquid	Endothall Dipotassium Salt	40.3	S,A
Granules	Endothall Dipotassium Salt	10.1	S,A
Hydrothol 191™			
Liquid	Endothall Dimethylalkylamine Salt	53.0	S,A
Granules	Endothall Dimethylalkylamine Salt	11.2	S,A
Asgrow 2,4-D	2,4-d Dimethylamine Salt	47.4	F
Diquat Herbicide - H/A	Diquat Dibromide	35.3	S,F,E
Rodeo™	Glyphosate Isopropylamine Salt	53.5	E,F
Banvel 720™	Dicamba Dimethylamine Salt	12.82	E,F
	2,4-D Dimethylamine Salt	24.58	
Cutrine-plus™	Copper-Ethanolamine Complexes	9.0	A,S
Sonar™			
Liquid	Fluridone	10.0	S,E
Pellets	Fluridone	5.0	S,E
Casoron™	Dichlobenil	10.0	S
Terrestrial Applications	**Active Ingredient(s)**	**% of Active Ingredient**	**Use[1]**
Velpar L™	Hexazinone	25.0	D
Arsenal™	Pyridinecarboxylic Salt	27.6	D

[1]E = EMERGENT; F = FLOATING; S = SUBMERGED; D = DITCHBANK PLANT TYPES; OR A = ALGAE

FIELD SAMPLING

The field monitoring program consisted of four sampling sites on the Taylor Creek/ L-63N Borrow Canal system (Figure 2). The first site, upstream of the application area, was at the Cemetery Road bridge as it crosses Taylor Creek. The other three sampling sites were on the L-63N Borrow Canal at Debbie bridge, SR 70 bridge, and SR 710 bridge. On July 9, 1986 surface spraying of glyphosate started approximately one-half mile upstream of Debbie bridge and continued until the SR 70 bridge. The SR 710 bridge represented the downstream sampling station. The glyphosate formulation used was Rodeo™ in combination with Ortho X-77™ as a surfactant. The maximum rate of 6 pints per acre (7 l/ha) or 4.05 pounds of active ingredient per acre (4.54 kg/ha) was applied to the aquatic vegetation, mostly duckweed, along the side of the canal in an area approximately nine meters wide. Surface water and sediment samples were taken the day before spraying (July 8), 18 hours later (July 10), one week later (July 16), and two weeks later (July 23).

Both water column and sediment samples were placed in glass containers specifically prepared for herbicide sampling and placed on ice. The water column samples were surface grab samples. The top layer of sediment was obtained using a petite Ponar dredge. Disposable rubber gloves were worn while taking any samples.

Water colum samples were taken at SR 70 in clean 40 ml vials for Microtox™ analysis before glyphosate spraying, 18 hours after spraying, and one week later.

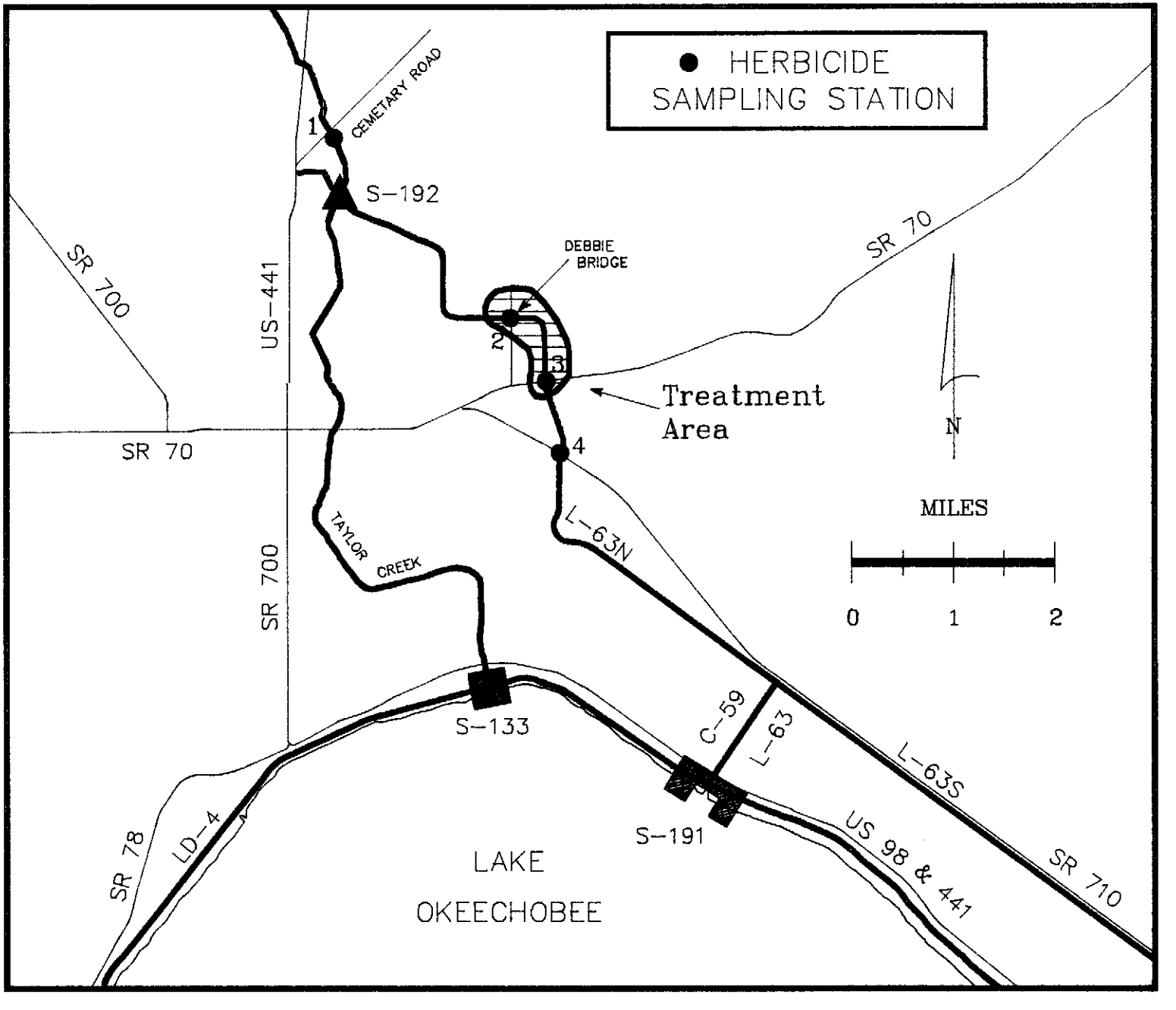

FIGURE 2. AQUATIC WEED CONTROL PROGRAM SAMPLING SITES

EQUIPMENT AND LABORATORY PROCEDURES

A high performance liquid chromatography (HPLC) technique was employed by the University of Miami, Division of Chemical Epidemiology laboratory, for the detection of glyphosate in the water and sediment samples. The technique utilized is a modification of the method developed by Moye et al. (1983). Water samples were filtered through a 0.45 micron filter and directly injected on the HPLC column without further cleanup. The sediment samples were air dried and then extracted with 0.1 N HCl. The extract was evaporated and passed through a 22 mm diameter column filled with 100 gms of ion exchange resin. The first 100 mls of eluate are discarded with the remainder being concentrated, filtered, and finally injected onto the HPLC column.

The ion pair eluant consisted of a dilute phosphoric and sulfuric acid solution. This solution was pumped by a Waters pump (Milford, MA) to a Aminex A-27 column (anion exchange, 25 cm X 4.0 mm ID) (Bio-Rad Laboratories, Richmond, CA) set at 70°C. The injector contained a 20 ul loop which allowed an injection of a 20 ul volume of sample. A Kratos URS 051 dual pump postcolumn reactor was used for derivatization. A calcium hypochlorite solution acted as an oxidizing agent to oxidize the glyphosate to the primary amine. Orthophthalaldehyde solution in borate buffer attaches to the primary amine oxidized by the calcium hypochlorite.

A Kratos Spectroflow 980 fluorescence detector set at 230 nm with a 418 nm emission cutoff filter was used for the derivatized glyphosate detection.

A Microtox™ Model 2055 Toxicity Analyzer System (Microbics Corporation, CA, USA) was used to determine relative toxicity of the herbicide treated water. Undiluted samples were osmotically adjusted with Microtox™ Osmotic Adjusting Solution (MOAS) to provide a 2% NaCl environment. A 2:1 serial dilution for testing yielded a final assay concentration range of 1 to 1/8. Duplicate determinations were utilized during the bioassay procedure.

RESULTS AND DISCUSSION

All the water and sediment samples were below the minimum detection limit (MDL) of 20 and 40 ppb, respectively, of glyphosate (Appendix 1). Based on 4.54 kg/ha uniform application rate and assuming a one meter zone of mixing for the applied chemical, it can be calculated that a 454 ppb concentration of glyphosate would be present in the surface water at the time of application. Since this concentration is approximately ten times greater than the MDL achieved by the analytical methodology, sufficient quantities of applied glyphosate was present for quantification.

The rapid removal of the glyphosate could be attributed to degradation (microbial or photolytic), adsorption to the target aquatic plants or sediment, and dispersion from turbulent mixing or flow. Due to the relatively small area actually covered during the spraying process compared to the canal's actual width, the most prominent force responsible for the disappearance of the glyphosate not adsorbed to the target plant, or any other surface applied aquatic herbicide, would be the dispersion from the turbulent mixing or flow. The resulting dilution of the herbicide would help to eliminate any detectable quantities. During the sampling period, flow as represented by discharge at S-191, was present in the canal. The actual flow can not be calculated as S-191 also receives water from the south. Also, the L-63N Borrow Canal between S-192 and S-191 is not gauged for flow measurements. Another potential loss mechanism would be microbial degradation. Water and/or soil with high microbial content have a higher degradation rate (Bronstad and Friestal 1985); however, the actual microbial population in the borrow canal system is not known. Adsorption to suspended particulate matter does not appear to be a major loss mechanism as the turbidity is relatively low in the Taylor Creek/ L-63N Borrow Canal System (Ritter and Allen, 1982) and the total suspended solids for S-191 is relatively low (SFWMD, 1986). Any glyphosate loss to the sediments by adsorption was minimal, since no residues over 40 ppb were detected.

No previous contamination problem with glyphosate existed in this area since the pre-application samples were negative.

Since none of the samples had detectable glyphosate residues, the Microtox™ testing could determine only if the canal water was toxic and not ascertain the effect of the glyphosate. The results of testing the canal water showed it to be stimulatory to the test organism and not toxic. The stimulation of the test organism was possibly due to the nutrients present in the water column which provided an additional growth media for the test organism.

The use of glyphosate in this canal system does not appear to present any environmental or health problems since the dissipation rate is very rapid and no known previous contamination problems exist in the study area due to past use.

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APPENDIX A.

SUMMARY OF GLYPHOSATE RESIDUE AND FIELD DATA

TABLE A-1. CONCENTRATION OF GLYPHOSATE RESIDUES IN PPB FOR WATER SAMPLES

Station	Sampling Date			
	07/08	07/10	07/16	07/23
Cemetery Road	ND	ND	ND	ND
Debbie Bridge	ND	ND	ND	ND
SR 70	ND	ND	ND	ND
SR 710	ND	ND	ND	ND

ND= BELOW MINIMUM LEVELS OF DETECTION (20 PPB)

TABLE A-2. CONCENTRATION OF GLYPHOSATE RESIDUES IN PPB FOR SEDIMENT SAMPLES

Station	Sampling Date			
	07/08	07/10	07/16	07/23
Cemetery Road	ND	ND	ND	ND
Debbie Bridge	ND	ND	ND	ND
SR 70	ND	ND	ND	ND
SR 710	ND	ND	ND	ND

ND= BELOW MINIMUM LEVELS OF DETECTION (40 PPB)

TABLE A-3. FIELD DATA OF CEMETERY ROAD BRIDGE STATION

Sampling Date	Water Temperature °C	Dissolved Oxygen ppm	Specific Conductivity µmhos/cm	pH
07/08	27.5	2.4	373	6.4
07/10	29.5	2.0	345	6.5
07/16	29.5	1.3	700	6.4
07/23	29.5	0.3	522	6.7

TABLE A-4. FIELD DATA OF DEBBIE BRIDGE STATION

Sampling Date	Water Temperature °C	Dissolved Oxygen ppm	Specific Conductivity µmhos/cm	pH
07/08	27.9	3.4	268	6.3
07/10	28.8	1.7	314	6.5
07/16	29.7	2.5	422	6.3
07/23	29.8	0.1	481	6.6

TABLE A-5. FIELD DATA OF SR 70 BRIDGE STATION

Sampling Date	Water Temperature °C	Dissolved Oxygen ppm	Specific Conductivity µmhos/cm	pH
07/08	27.8	1.7	361	6.2
07/10	29.0	1.4	333	6.5
07/16	29.5	1.7	402	6.2
07/23	30.1	0.7	474	6.6

TABLE A-6. FIELD DATA OF SR 710 BRIDGE STATION

Sampling Date	Water Temperature °C	Dissolved Oxygen ppm	Specific Conductivity µmhos/cm	pH
07/08	27.9	1.9	260	6.2
07/10	28.7	2.0	328	6.5
07/16	29.7	2.1	391	6.2
07/23	29.9	0.9	453	6.7

APPENDIX B.
COMPOUND SELECTION INFORMATION

APPLICATION QUANTITIES

Table B-1 lists the amount of each herbicide used in 1984 by the District and the calculated amount of applied active ingredient. The calculated amount of applied active ingredient provides a means of ranking the herbicides as to the quantity of active ingredient entering the environment. As seen from Table B-1, the major herbicide used is liquid Aquathol K™ (endothall). This is followed by 2,4-D, Rodeo™ (glyphosate), and diquat. The remainder of active ingredients applied are at least six times less.

DEGRADATION ANOMALIES

The first step in the literature review was to determine if any of the active ingredients have been studied in the south Florida environment and if they have any unusual physical/chemical properties. The detailed results of the review for each individual compound follows. Properties which would make a chemical a candidate for not degrading as expected include a long half-life in the water column or sediment; or a tendency for sorption or the lack of it.

Endothall

The herbicidal properties of endothall (7-oxabicyclo(2.2.1) heptane-2,3-dicarboxylic acid) have been known since 1948, with the development of the aquatic herbicide formulations in the early 1960s. The mode of action of endothall is not clearly defined. Simsiman et al. (1976) summarized several studies implicating inhibition of protein synthesis, retardation of lipid metabolism, and disruption of cell membranes. Unlike most pesticide and herbicide chemicals, endothall contains only carbon, hydrogen, and oxygen. Rather than being applied as the free acid, endothall is converted to its inorganic or amine salts. These salts are then applied as water concentrates for aquatic use, making the use of organic solvents or emulsifiers unnecessary. The two formulations, the dipotassium salt and the dimethylalkylamine salt, have both terrestrial and aquatic applications.

TABLE B-1. QUANTITIES OF HERBICIDES USED IN 1984

Herbicide	Quantity Used in 1984	Rank	Quantity AI[1] Per Application Unit		Pounds AI Applied	Rank
Aquathol K™						
Liquid	14,886.2 G[2]	1	3	P AI/G	44,658.6	1
Granuels	520.0 P[3]	8	0.072	% AI/P	37.4	10
Hydrothol 191™						
Liquid	1,357.7 G	6	2	P AI/G	2,715.4	5
Granules	13.5 P	10	0.05	% AI/P	0.7	12
2,4-D	8,415.7 G	2	3.8	P AI/G	31,979.7	2
Diquat Herbicide-H/A	6,292.8 G	3	2	P AI/G	12,585.6	4
Rodeo ™	3,393.7 G	4	4	P AI/G	13,574.8	3
Banvel 720 ™						
Dicamba	1,406.4 G	5	1	P AI/G	1,406.4	7
2,4-D	1,406.4 G	5	1.9	P AI/G	2,672.2	6
Cutrine-plus ™	1,313.5 G	7	0.909	P AI/G	1,194.0	8
Sonar™						
Liquid	6.0 G	11	4	P AI/G	24.0	11
Pellets	0.0	12	0.05	% AI/P	0.0	13
Casoron™	0.0	12	0.1	% AI/P	0.0	13
Velpar L™	444.0 G	9	2	P AI/G	888.0	9
Arsenal™	0.0	12	2	P AI/G	0.0	13

[1]AI = ACTIVE INGREDIENT [2]G = GALLONS [3]P = POUNDS

Holmberg and Lee (1976) found endothall applied at 5 mg/l had no effect on the water chemistry and dissolved oxygen, under natural conditions, at study ponds in Wisconsin. Residues in the water column decreased beyond the detection limit (0.1 mg/l) after 18 days. It was also concluded that the 5.0 mg/l application rate is a sublethal dosage for bluegills, as no noticeable mortalities occurred in the treatment pond.

Gatun Lake, Panama, was the study site for determining the effectiveness of the two endothall formulations on hydrilla (Westerdahl, 1983). Application rates were selected to bracket the actual endothall concentration required to achieve hydrilla control. The projected endothall concentrations in water at the aforementioned application rates were approximately 1.0, 1.5, and 2.0 ppm. By post-treatment day seven, less than 0.01 ppm of endothall was detected in the water column. Endothall residues in the sediment samples from the dipotassium salt formulation study site were below minimum detection limits by post-treatment day seven. The dimethylalkylamine salt formulation, however, remained significantly high, i.e. >1.00 ppm for more than 21 days. No long-term adverse environmental impacts to nontarget organisms or direct effects on water quality were observed as a result of either endothall formulation.

Reinert and Rodgers (1984) calculated an aquatic half-life of 2.8 days for the dipotassium salt. These authors determined that in the aquatic environment sorption, volatilization, hydrolysis, photolysis, and oxidation play minor roles in the fate process, while biotransformation has the greatest effect on the degradation of endothall. They concluded that the relatively high concentration of endothall required for acute toxicity, a low sorption coefficient, and low environmental persistence combine to make endothall a candidate for the control of nuisance aquatic vegetation.

Armstrong (1974) concluded, after a review of the literature, that endothall does not persist in the environment and the levels required to control aquatic vegetation do not seem to be harmful to either fishes or fish-food organisms. A control program using endothall would be both ethical and defensible.

Endothall is readily broken down by microorganisms which incorporate its constituents (carbon, hydrogen, and oxygen) into natural products. Beckmann et al. (1984) determined that at recommended rates, the annual applications of the dipotassium salt of endothall does not appear to be detrimental to the aerobic, heterotrophic, bacterial populations of a Illinois pond ecosystem. Studies using endothall show that there is no bioaccumulation in the aquatic food chain (Freed and Gauditz, 1961; Walker, 1963).

The rapid degradation of endothall does indicate that this chemical will not persist in the environment and therefore would be a poor candidate for monitoring. The dipotassium salt of endothall has a wide margin of safety to fish, being non-toxic to fish at levels 10 to 100 times the maximum recommended rate. However, the dimethylalkylamine salt is toxic to fish, estuarine, and marine organisms and extreme care must be used in the application of this chemical.

2,4-D

The active ingredient 2,4-D (2,4-dichlorophenoxy acetic acid) has been used as a herbicide since the mid-1940s. The biochemical causes of its phytotoxic properties remain unknown; although investigation has shown that it causes abnormal growth response and affects respiration, food reserves, and cell division analogous to the typical auxin activity (Beste, 1983). It is presumed the phytotoxic properties deactivate enzyme systems by interacting with proteins. The majority of the registrations cover application of formulations of the 2,4-D acid, its four inorganic salts, its greater than 20 alkyl- and alkanol-amine salts, or its greater than 20 esters. The amine in largest production is the dimethylamine salt (US DHHS, 1983). 2,4-D is among the most extensively used herbicides, having major turf, forestry, industrial, and aquatic uses as well as crop and pastureland uses.

Numerous studies have investigated the aquatic fate of 2,4-D. Schultz (1974) conducted studies to determine the uptake and dissipation of the dimethylamine salt of 2,4-D in water, sediment, and fish. His studies were conducted in 11 ponds located at three different geographical and ecological sites. Residues of 2,4-D salt declined to less than 0.005 mg/l in samples taken 28 days after application in Florida and Georgia pond waters. Sediment residues were never found to be higher than 0.5 mg/kg in the Florida and Georgia ponds. Foret and Barry (1979) presented data that 2,4-D residues at all sampling locations in Louisiana (when applied for water hyacinth control in a slow moving stream) were always well below the 0.1 mg/l level established by the EPA for potable water. This work verified the results of a large scale application of 2,4-D for water hyacinth control on the St. Johns River in 1975 (Joyce and Sikka, 1977). They found 2,4-D levels ranged from nondetectable to 1.3 µg/l following spraying, and reported no apparent correlation between quantities of 2,4-D applied and the residues detected in the water.

The hydrolysis of selected 2,4-D esters to the free acid occurs rapidly in aqueous solutions. 2,4-D also degrades in water in the presence of UV light, forming 2,4-dichlorophenol, 4-chlorocatechol, 2-hydroxy-4-chlorophenoxyacetic acid, 1,2,4-benzenetriol and polymeric humic acids (US DHHS 1983). Reported half-lives in environmental waters range from a few days to several months depending on factors such as temperature, pH, light intensity, formulation, and oxygen concentration. 2,4-D is degraded in the environment at a relatively rapid rate, with residue half-lives generally not exceeding several weeks in plants, soil, and water. It is rapidly eliminated by animals and is not bioaccumulated. This low environmental persistence, and the potential for 2,4-D entering the study site from agricultural applications, makes 2,4-D a poor candidate for monitoring.

Diquat

Diquat (diquat dibromide or 6,7-dihydrodipyrido (1,2-a:2',1'-c) pyrazinediium dibromide) is a non-selective herbicide developed in the early 1960s. Diquat's herbicidal activity is due to the inhibition of photosynthesis by disrupting the light reactions and blocking the photosynthetic electron transport mechanism (Buchel, 1983). Diquat is soluble in water, but is subject to hydrolysis in the presence of alkaline materials, including alkaline waters. Diquat is highly susceptible to ultraviolet degradation, resulting in a loss of diquat by photochemical decomposition on sprayed leaf surfaces and on dead and decaying vegetation.

Due to its cationic nature, an important and unique property of diquat is its very rapid and complete inactivation by soil. (Beste,1983). The adsorption of diquat in soils, by reaction with humic acids and by normal Langmuir type adsorption onto organic matter and soil particles, is a weaker binding than with clay minerals in soils; however, even in this case, fairly high concentrations in the soil are required to give phytotoxic concentrations of diquat in the soil water. Additionally, Bowner (1982) demonstrated that in the water column, suspended particulate matter can adsorb diquat and completely inactivate it. After the suspended particulate matter adsorption capacity was saturated, the herbicide could then be effective if sufficient amounts were applied.

Experiments with microorganisms in culture media have shown that certain of these are capable of decomposing diquat in the absence of soil. However, they degrade bound diquat with difficulty or not at all. When bound to soil, diquat is very persistent but biologically unavailable. Since leaching from soil is apparently negligible, diquat residues are also considered immobile (Burns and Audus, 1970; Simsiman et al., 1976).

Several papers describe residual phytotoxicity of diquat in various soils and soil components even when these herbicides were adsorbed at levels well below the adsorptive capacity of the soil system (Coats et al., 1966; Weber and Scott, 1966; Weber et al., 1969a, b; Burns and Audus, 1970; Damanakis et al., 1970). Laboratory experiments with a relatively complex herbicide-aquatic plant-soil test system do suggest that residual phytotoxicity may occur in small, sheltered, and enclosed bodies of water depending on the type of bottom sediment (Birmingham and Colman, 1983). Furthermore, the binding capacity of the sediments need not be exceeded before residual phytotoxicity becomes apparent.

Diquat's rapid disappearance from water is attributed largely to adsorption by sediments, suspended particulate matter, and aquatic plants i.e. suitable sorbents (Frank and Comes, 1967). Most of the diquat administered to water ultimately accumulates in the sediment, either directly or following release from decaying plant or animal material, at the water-sediment interface (Simsiman et al., 1976). Diquat residues have been shown to accumulate and persist in aquatic sediments for long periods of time. Frank and Comes (1967) found diquat residues of 24 ppm in the sediment 160 days after an initial application rate of 0.62 ppm. Simsiman and Chesters (1976) determined that diquat, added at 1.5 ppm to a weed-infested simulated lake impoundment in Wisconsin, was sorbed initially by the weeds. Following rapid weedkill, profuse proliferation of microorganisms occurred, promoting degradation of the herbicide sorbed on the decomposing weeds. Within 22 days, diquat degraded extensively to water-soluble products (32%) and only minimal sediment adsorption occurred (19%). However, in weed-free sediment water incubation systems, diquat in water at 5 ppm was adsorbed rapidly by the sediments, and the major portion of the herbicide persisted in its intact form throughout the experiment (up to 180 days).

Due to its tenacity for binding to the sediment/soil interface and a lack of microbial degradation once bound, which results in a long residue half-life, diquat is a potential candidate for monitoring.

Glyphosate

Rodeo™, the isopropylamine salt of glyphosate (N-(phosphonomethyl) glycine), is a relatively new compound developed in 1970. The active ingredient glyphosate has both terrestrial and aquatic applications with the emergent type aquatic weeds

being controlled during aquatic applications. Rodeo uses the biological process known as translocation, the means by which sugars and other materials are circulated throughout living plants, to spread to all parts of the treated weed. The actual mechanism of action is unknown, but the herbicide appears to inhibit the aromatic amino acid biosynthesis pathway and may inhibit or repress chlorismate mutase and/or prehenate dehydratase (Beste, 1983).

The results of field studies on 11 different soils, covering a full range of soil types and geographic areas, indicated an average half-life for glyphosate of two months. Other studies have reported half-lives of 17-19 weeks for sandy soil and three weeks in silt loam (Ghassemi et al., 1982). Glyphosate is strongly adsorbed and not readily leached in many soil types. This adsorption is considered the initial step for inactivation in soil. Glyphosate adsorption, which occurs through the phosphonic acid moiety, begins almost immediately after application and increases slowly after one hour (Sprankle et al., 1975b). The phosphate level appeared to be the most important factor in determining the quantity of glyphosate adsorbed. As the quantity of phosphate in the soil increased, glyphosate adsorption decreased, whereas pH did not seem to affect adsorption. Sprankle et al. (1975b) determined glyphosate mobility in the soil is very limited and is affected by pH, phosphate level, and soil type. Up to 45% of the ^{14}C-glyphosate was degraded to $^{14}CO_2$ in 28 days by a Conover sandy clay loam soil, but less than 20% was degraded in the Toledo clay loam soil. Hance (1976) commented that this is not a particularly rapid rate of degradation and that this observation is inconclusive in that the residual unchanged glyphosate was not measured. Hance (1976) concluded, in conjunction with reports in the literature of glyphosates degradation rate and phytotoxicity, that the low activity of glyphosate in the soil is the consequence of a combination of moderate adsorption and low intrinsic toxicity when made available to the root system. Other studies by Sprankle et al.(1975a) have shown that adsorption of glyphosate by sandy clay loam soils decreases with increasing pH at higher application rates. Glyphosate applied at 25 times the proposed use rates was rapidly inactivated by the soil. Using autoclaved soil, glyphosate was still rapidly inactivated by the soil, suggesting that the rapid soil inactivation was not due to microbial degradation, but adsorption to the soil particles.

Adsorption of gylphosate to soil reduces its mobility through leaching and surface runoff. Comes et al. (1976) investigated leaching of glyphosate from banks of irrigation canals treated with glyphosate. Neither glyphosate nor its primary soil metabolite, aminomethylphosphonic acid (AMPA), were detected in the first flow of water through two canals which had been treated 23 weeks earlier with an application (5.6 kg/ha) of "Round-up." This application had been made to the ditchbanks when the canals were dry. Soil samples collected the day before the canals were filled contained about 0.35 ppm glyphosate and 0.78 ppm AMPA in the 0 to 10 cm layer. In laboratory runoff studies conducted by Rueppel et al. (1977), maximum runoff of less than 2×10^{-4} kg/ha was observed from Ray, Drummer, and Norfolk soil beds inclined at 7.5 degrees and treated with 1.12 kg/ha glyphosate and subjected to three artificial rainfalls. Rueppel et al. (1977) concluded that glyphosate possesses no propensity for leaching.

Several laboratory studies have indicated that microbial degradation of glyphosate in soil is rapid (Sprankle et al., 1975b; Rueppel et al., 1977). In shake flask tests conducted by Rueppel et al. (1977), between 53% and 61% of ^{14}C-labeled glyphosate degraded within 28 days in Ray silt loam, Drummer silty clay loam, Lintonia sandy loam, and Norfolk sandy loam soil with organic matter contents of 1.0%, 6.0%, 1.1%, and 1.0%, respectively.

Based on limited laboratory and field data, volatilization and photodecomposition do not make significant contributions to the loss of glyphosate from soil following application (Rueppel et al., 1977). Microbial degradation is the major route of degradation of glyphosate in water; a half-life of approximately seven weeks has been reported (Ghassemi et al., 1982). Glyphosate does not degrade in water via chemical routes. No degradation was observed of 0.1 ppm at pH 4 to 7.3 after incubation for 49 days in the dark; or of 25 or 250 ppm at pH 3.6 and 9 following incubation at 5° and 35° C in the dark for 32 days. The rate of photodegradation in water is considered negligible based on the rate of glyphosate photodegradation in soil.

Its relatively long half-life in water and soil, and the significant amount applied, makes glyphosate a possible candidate for monitoring.

Dicamba

Banvel 720™ is a combination of the dimethylamine salt of dicamba and 2,4-D. The active ingredient 2,4-D was discussed above. The active ingredient dicamba was initially registered in 1967. Like 2,4-D, dicamba (3,6-dichloro-o-anisic acid) exhibits properties of an auxin-like plant growth regulator (Buchel, 1983). Dicamba is adsorbed to peat, but not appreciably adsorbed to soils ranging from heavy clay to loamy sand. More dicamba is adsorbed

on clays, especially kaolinite, than on sands (Burnside and Lavy, 1966). Dicamba is readily mobile in soils ranging from clay to loamy sand. Dicamba moves with the wetting front in soils ,including upward movement with subirrigation (Harris, 1964). The average half-life in soil is 1 to 6 weeks; however under conditions of low soil moisture and rainfall, persistence may be longer. Dicamba dissipated more rapidly from silty clay loam than sandy loam, from topsoil than subsoil, and from high than low incubation temperature (Hahn et al., 1969). Dicamba is more persistent in soil than phenoxy herbicides such as 2,4-D (Friesen, 1965; Harris et al., 1969). Microbial degradation is primarily responsible for soil losses as data from sterile and nonsterile soil samples indicate that larger losses of dicamba are due to metabolism rather than to volatilization (Beste, 1983). In humid regions, dicamba may be leached out of the zone of activity in 3 to 12 weeks.

Dicamba dissipated most rapidly from water under non-sterile, lighted conditions. In a test pond in Texas, an initial concentration of 11 ppm required 40 days for dissipation (Scifres et al., 1973). The calculated average loss was about 1.6 ppm/day for the study period with most rapid loss the first seven days following treatment of the ponds. Additionally, data from greenhouse studies supports the importance of microbial activity in the degradation of dicamba in sediments. Generally, although slightly more persistent than 2,4-D, dicamba does not appear to be as persistent as glyphosate. Based on this conclusion and the relatively small quantities applied, dicamba would not be a good candidate for monitoring.

Fluridone

Fluridone (1-methyl-3-phenyl-5-[3-(trifluoromethyl)phenyl] -4-(1H)-pyridinone) is a relatively new herbicide developed in the mid-1970s. Fluridone is used to control most submerged and emerged aquatic plants by the inhibition of carotenoid synthesis which ultimately results in the formation of albescent tissue in susceptible plants (Beste, 1983). The phytotoxic effects of fluridone on aquatic plants are unique in that chlorosis is noted 7-10 days after treatment; however, thirty to sixty days are necessary before weed control is observed. This slow herbicidal response causes minimum effect on the water quality (Arnold, 1979). Specifically, because of the slow decline in vegetation, the dissolved oxygen concentration is not dramatically decreased. It is assumed that the mature leaves and stems continue photosynthesis and production of oxygen until death (anonymous, 1981).

Fluridone is moderately susceptible to decomposition by ultraviolet irradiation in an aqueous solution but is stable to hydrolysis at pH 3, 6, and 9 (McCowen et al., 1979). Field studies in Michigan and New York indicated that fluridone exhibited a half-life of 14 days or less in pond water with application rates of 0.1 and 0.3 ppm, respectively. At the Michigan site, fluridone was below detection limits (0.0005 ppm) after 54 days while water residues of 0.023 ppm were still present at the New York site after 84 days. Factors contributing to the dissipation of fluridone from the water included rapid uptake by the aquatic plants, adsorption onto the hydrosoil, and photodegradation. Estimated half-lives were not calculated for the hydrosoil at these study sites where a 0.035 ppm fluridone residue was still present after 54 days and 0.078 ppm residue present after 84 days at the same Michigan and New York sites, respectively. Fluridone levels did not accumulate in fish from the ponds in Michigan. Twenty-seven days after application, no detectable residue was present at a sensitivity of 0.01 ppm.

In an unspecified site studied by Arnold (1979), water and hydrosoil had detectable residues of 0.011 and 0.031 ppm, respectively, 187 days after application of approximately 0.3 ppm fluridone. Muir et al. (1980) reported half-lives in the water column of a Canadian pond from 4 (at 0.7 ppm) to 7 days (0.07 ppm). The change in fluridone concentration with time was logarithmic showing good agreement with the integrated form of first-order kinetic rate equations for about 12 weeks after application. Fluridone levels in water samples taken from 12 to 17 weeks after treatment were relatively constant, possibly reflecting equilibrium with residues in the hydrosoil. The rate of disappearance of fluridone in the present study was similar to that reported by West et al. (1979) who found an average half-life of 5 days in water of several ponds and lakes under several different climatic conditions. In general, the ponds located in a temperate climate, New York and Michigan, had the longest half-lives, while the half-lives calculated from the sub-tropical Florida study ponds were less. The study areas of a tropical climate in Panama had the shortest half-life. The half-life of fluridone in the water column is much shorter than that for simazine (Mauck et al., 1976), terbutryn (Muir et al., 1979), or dichlobenil (Rice et al., 1974). Endothall and diquat (Sikka and Rice, 1973; Simsiman and Chesters, 1976) have been observed to have somewhat shorter disappearance times from the water columns of lakes, small ponds, or simulated lake impoundments.

Muir et al. (1980) also reported fluridone half-lives in the hydrosoil to be greater than one year since

relatively little change in herbicide concentration was seen after the maximum concentrations were reached. Similar persistence in bottom mud was noted by West et al. (1979) who monitored fluridone residues for up to 12 months after treatment at sites in Florida. The Orlando treatment pond had hydrosoil residues of 0.356 kg/ha after 364 days from an initial application of 2.0 kg/ha. Fluridone residue following application at 1.1 kg/ha to a pond in Hialeah was 0.056 kg/ha after 272 days but was reduced to no detectable residue by 364 days. The second Hialeah pond, with an application rate of 1.7 kg/ha had no detectable hydrosoil residue after 364 days but did have a water column residue of 0.003 ppm. The adsorption coefficients (Koc) of fluridone in the six Canadian hydrosoils investigated by Muir et al. (1980) indicates that the herbicide is most strongly sorbed to hydrosoils of high organic matter and silt content. Percent desorbtion was greatest from hydrosoils of lowest organic carbon content.

West and Parka (1981) studied the rate of fluridone dissipation from the water and hydrosoil of two ponds in central Indiana following application by two different methods. The data indicated that fluridone dissipated at a similar rate with both the surface and bottom application techniques. Half-lives determined from a least-squares line, obtained by plotting the concentration of fluridone versus the number of days after treatment on a semilogarithmic scale, were 21 and 26 days for the surface and bottom application, respectively. Only 4% of the initial fluridone concentration remained in the water of either pond 110 days after treatment.

The residue pattern of fluridone in the hydrosoil was also similar for both types of application. In both ponds, maximum fluridone residues in the hydrosoil were observed 14 days after treatment and were equivalent to 7% and 9% of the total amount of fluridone applied to the ponds. Fluridone was not detected in the hydrosoil of either pond 56 days after treatment.

Fluridone has a relatively long half-life. However, since this herbicide was not registered for use during this study, application of this chemical would not occur within the monitoring period of this program.

Dichlobenil

Dichlobenil (2,6-dichlorobenzonitrile) is an inhibitor of germination and of actively dividing meristems and acts primarily on growing points and root tips (Beste, 1983). The biological properties were first described in 1958. The mechanism of action is virtually unknown (Buchel, 1983). Hydrolysis to 2,6-dichlorobenzoic acid or the amide (both are also phytotoxic) has been excluded as the reason for their high herbicidal activity.

Dichlobenil is a member of the substituted benzonitrile family of herbicides with a relatively high volatility (vapor pressure 1.5×10^{-2} mm at 50° C) and low water solubility (18 ppm at 20° C). The downward movement of dichlobenil with water through the soil is extremely slow due to its low water solubility and adsorption on soil constituents. There is some additional transport of dichlobenil due to diffusion in the vapor phase. Soils with high humus contents need higher dosages. This can be explained by the fact that the adsorption of dichlobenil on soils is dependent on their contents of organic matter. In pure sand and on clay the adsorption is rather low. In soils dichlobenil is gradually broken down microbiologically into 2,6-dichlorobenzamide. The rate of this process depends on the soil type. In laboratory experiments with eight different soil types the half-life of dichlobenil varied between 1.5 and 12 months. Because of the relatively high volatility of dichlobenil and its co-distillation properties with water, loss of dichlobenil from the soil surface can be rapid. Under circumstances of high water evaporation from the soil (high temperature, wet soil, low relative air humidity) dichlobenil can evaporate very rapidly. From dry soil the evaporation of dichlobenil is dependent on soil types and temperature.

Van Valin (1966) reported that an application of the 50% wettable powder at 10 ppm to an Oklahoma pond resulted in <0.01 ppm residue in the water column 40 days after treatment and residues of 0.028 ppm in the sediment after 312 days . Several investigators (Frank and Comes, 1967 Cope et al., 1968) have reported that dichlobenil persists in the water and hydrosoil of treated ponds for 160 to 188 days following an application of the 4% granular formulation at recommended rates. Walsh and Heitmuller (1969) also reported on dichlobenil residues in a pond treated with the wettable powder formulation at 1.0 ppm. They found that the concentration of dichlobenil in the water and hydrosoil decreased steadily after treatment until negligible amounts were present after 64 days.

Ogg (1972) monitored dichlobenil residues from the two formulations in a man-made pond in Oregon. Residual levels of dichlorbenil in pond water and hydrosoil were compared after field applications of wettable powder and granular formulations to separate ponds at 10.0 lb/surface acre (0.6 ppmw, parts per million by weight, in the water). Maximum residual concentrations in the water, reached 4 and 5 days after treatment with wettable powder and

granules, respectively, were 1.00 and 0.68 ppmw. After 15 days, the residual concentrations were approximately the same and both decreased steadily to the detection limit of 0.001 ppmw after 126 days (last sampling date). The maximum concentration of dichlobenil in the hydrosoil was 1.472 ppmv, parts per million by volume, 6 days after treatment with wettable powder and 3.700 ppmv 1 day after treatment with the granules. Residues in the hydrosoil of the two ponds did not reach similar levels until 34 days after treatment. The residual concentrations from the wettable powder and granular treatment had decreased to 0.039 and 0.025 ppmv, respectively, 126 days after treatment. The persistence of dichlobenil in pond water and hydrosoil was similar whether applied as a granular or a wettable powder formulation. Dichlobenil has a relatively long half-life; however, the small quantities applied preclude this herbicide as a possible monitoring candidate.

HERBICIDE TOXICITIES

The acute and chronic toxicities for the active ingredients are given for some representative species in Tables B-2 and B-3 respectively.

The acute toxicity is the adverse effect(s) of a substance administered as a single dose or in multiple doses over a short period (generally 24 hours or less). The test animals are then observed for 14 days after exposure for immediate and delayed toxicities. The chronic toxicity is the adverse effect(s) produced by a substance administered repeatedly to animals over a long period of time, generally 1/2 of the lifespan or longer. For both the acute and chronic toxicity, the lower the value the more poisonous or toxic the chemical.

The rat toxicity provides a relative measure of toxicity which can be extrapolated to measure the potential human toxicity. Herbicides with a LD50 from 50 to 499 are considered moderately toxic. Endothall, 2,4-D, and diquat are in this class designation. Slightly toxic compounds, with a LD50 between 500 and 4,999, are glyphosate, technical dicamba, and dichlobenil. The almost non-toxic compounds, fluridone for example, have a LD50 from 5,000 to 14,999. However, none of the active ingredients listed on Table B-2 are considered very toxic, i.e. LD50 less than 49 mg/kg.

TABLE B-3. CHRONIC TOXICITIES FOR THE ACTIVE INGREDIENTS

Active Ingredient	Oral Rat PPM
Endothall	
Dipotassium Salt	>300[1]
Amine Salt	-
2,4-D	1,250[1]
Diquat Dibromide	25[1]
Glyphosate	30[1]
Dicamba Amine Salt	2900[1]
Fluridone	200[2]
Dichlobenil	20[1]

1Beste 1983
2Anonymous 1981

TABLE B-2. ACUTE TOXICITIES FOR THE ACTIVE INGREDIENTS

Active Ingredient	Oral Rat LD50 MG/KG	Largemouth Bass LC50 PPM	Bluegills PPM
Endothall			
Dipotassium Salt	125.[1]	96-HR 125[3]	96-HR TL50 160[4]
Amine Salt	206.[1]	96-HR 0.3[3]	
2,4-D	300.[1]		
Diquat Dibromide	230.[1]		
Glyphosate	5600.[1] 4900.[2]		96-HR LC50 120[1]
Dicamba Amine Salt	2.74[1]		
Technical	1040.[2]		
Fluridone	>10,000.[1]		96-HR LC50>9<12.5[1]
Dichlobenil	3160.[1]	20[1]	15[1]

[1]Beste 1983 [2]Thomson 1983 [3]Walker 1963 [4]Schultz 1973