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DYNAMAC
CORPORATION

DIQUAT DIBROMIDE

Final Report

Task 1: Review and Evaluation of Individual Studies

Contract No. 68-01-6679

DECEMBER 31,1985

Submitted to:
Environmental Protection Agency
Arlington, VA 22202

Submitted by:
Dynamac Corporation
Enviro Control Division
The Dynamac Building
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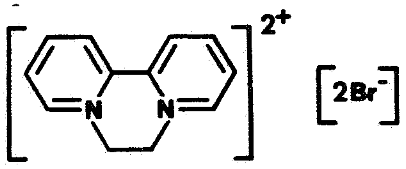
Rockville, MD 20852

DIQUAT DIBROMIDE

AQUACIDE, DEXTRONE, REGLONE, REGLOX, WEEDTRINE-D



6,7-Dihydrodipyrido(1,2-a:2',1'-c)pyrazinediium dibromide

Table of Contents

Study

1 Riley, D., R. Gratton, and W. Wilkinson. 1972. Diquat: Physiochemical behaviour and herbicidal activity of residues in soil: AR 2372 A. Unpublished study received Dec. 21, 1982 under 239-2247; prepared by ICI Plant Protection, Ltd., Eng., submitted by Chevron Chemical Co., Richmond, CA; CDL:249102-Q. (00121315)

2 Wilkinson, W. 1980. Paraquat and diquat: long-term high-rate trial, Frensham, U.K. 1. Management of site, effects on crops and weeds and residues in crops: Report Series RJ 0013 B. Unpublished study received June 4, 1980 under 239-2186; prepared by ICI, submitted by Chevron Chemical Co., Richmond, CA; CDL: 242577-A. (00052389)

Gowman, M.A., D. Riley, and S.E. Newby. 1980. Paraquat and diquat: long-term high-rate trial, Frensham, U.K. 2. Persistence and Movement in soil, and glasshouse bioassays: Report Series RJ 0014 B. Unpublished study received June 4, 1980 under 239-2186; prepared by ICI, submitted by Chevron Chemical Co., Richmond, CA; CDL:242577-B. (00052390)

3 Yeo, R.R. 1967. Dissipation of diquat and paraquat and effects on aquatic weeds and fish. Weeds 15:42-46. Also <u>In</u> unpublished submission received Aug. 22, 1977 under 239-1663; submitted by Chevron Chemical Co, Richmond, CA; CDL:231431-R. (00068232)

4 Schreck, C., R. Corning, and C. Berry, et al. 1974. Aquatic plant control using herbicides in a large potable water supply reservoir. Annual rept., July 1, 1973--June 30, 1974: Contract No. DACW65-74-C-0013. Virginia Polytechnic Institute and State Univ., Dept. of Fisheries and Wildlife Sciences for U.S. Dept. of the Army, Corps of Engineers; unpublished study; CDL:247354-B. (00100609)

5 Upton, B.P., P. Hendley, and M.W. Skidmore. 1985. Diquat: Hydrolytic stability in water at pH 5, 7, and 9. ICI Plant Protection Division, Jealotts' Hill Research Station, Bracknell, Berkshire, UK. Accession Nos. 259950, 259951. (No MRID)

(TDR03B) DATA EVALUATION RECORD PAGE 1 OF 8

CASE GS0288 DIQUAT DIBROMIDE STUDY 1 PM --

CHEM 032201 Diquat Dibromide

BRANCH EFB DISC --

FORMULATION 90 - FORMULATION NOT IDENTIFIED

FICHE/MASTER ID 00121315 CONTENT CAT 01

Riley, D., R. Gratton, and W. Wilkinson. 1972. Diquat: Physiochemical behaviour and herbicidal activity of residues in soil: AR 2372 A. Unpublished study received Dec. 21, 1982 under 239-2247; prepared by ICI Plant Protection, Ltd., Eng., submitted by Chevron Chemical Co., Richmond, CA; CDL:249102-Q.

SUBST. CLASS = S.

DIRECT RVW TIME = 6 (MH) START-DATE END DATE

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APPROVED BY:
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SIGNATURE: DATE:

CONCLUSION:

Mobility - Leaching and Adsorption/Desorption

This study is scientifically invalid because there was no standard curve to relate the growth inhibition of wheat to the concentrations of the test substance. In addition, study would not fulfill EPA Data Requirements for Registering Pesticides because the test substance was uncharacterized, complete soil characteristics were not provided, and K_d values were not reported.

MATERIALS AND METHODS:

Experiment 1

Samples (10 g) of four soils (Table 1) were shaken overnight with 200 ml of solutions of diquat dibromide (test substance uncharacterized, source unspecified) at 100, 200, 300, 400, 600, 800, 1000, and 1200 ppm. The suspensions were centrifuged and the supernatants were analyzed with a wheat bioassay by suspending ~5 pregerminated wheat seeds (Triticum aestivum var. Kolibri) in nylon gauze immediately above 100 ml of the solutions. The wheat seedlings were harvested after 2 weeks growth in a glasshouse. Root and shoot lengths and shoot weights were measured in relation to controls.

Experiment 2

Samples (2 kg) of four soils (Table 1) were mixed with 200 ml of solutions of diquat dibromide (test substance uncharacterized, source unspecified) at 100-1200 ppm (Figure 3), placed in a plastic pot (18 cm diameter) and leached 3 times with 1 liter of distilled water to remove soluble salts. After partial drying, 1.3 cm of soil was removed and ~50 wheat seeds were planted and covered with the removed soil. The pots were watered with a nutrient solution and kept in a greenhouse with 16 hours of daylight. There were 3 replicates of each treatment plus controls. Shoots were harvested after 4-5 weeks, dried at 80 C and weighed in comparison to controls. After harvest, the Sandy Hills sandy loam and the Methwold fen peat soils were replanted with wheat, watered with a nutrient solution and grown in the greenhouse as with the first crops. Roots and shoots were harvested after 5 weeks. The Broadrick's sandy loam was replanted with radish (Raphanus sativus, var. Sutton Scarlet Globe), which were thinned to 6 plants/plot after emergence. Whole plants were harvested after 5 weeks and yields were compared to controls.

In a related experiment, the Sandy Hills sandy loam soil (10 g) from the pot experiment was bioassayed with the floating aquatic plant, Lemna polyrhiza, by placing the treated soil in beakers with 100 ml of distilled water plus 1 ml of Hoagland's nutrient solution and floating ~5 plants on the water surface. One-half of the beakers were also treated with a 0.1 N calcium chloride solution. Distilled water was added to maintain the water volume. The Lemna was harvested after 7 days, dried at 80 C, weighed, and compared to controls.

REPORTED RESULTS:

Experiment 1

Figures 1 and 2 depict the reduction in shoot and root length of wheat grown in soils treated with solutions of diquat dibromide. Plant growth was reduced most in the peat soil and least in the Broadrick's sandy loam.

Experiment 2

Figure 3 depicts the reduction in shoot weight of wheat grown in soils treated with diquat dibromide. Shoot weight was reduced most in the peat soil and least in the Broadrick's sandy loam. In the fen peat soil ~20 ppm of diquat dibromide phytotoxic residues reduced the dry weight of wheat shoots (Table 2), whereas in the Broadrick's sandy loam 1100 ppm of diquat dibromide phytotoxic residues reduced the growth of wheat (first crop) and radish (second crop).

DISCUSSION:

1. A standard curve relating growth inhibition of wheat to the concentration of diquat dibromide in the soil was not established. Therefore, quantitative data on the mobility of diquat dibromide was not available.
2. The test substance was uncharacterized.
3. Complete soil characteristics, such as CEC, were not reported.
4. Soil/water relationship (K_d) values were not provided.
5. A nonspecific bioassay method was used.

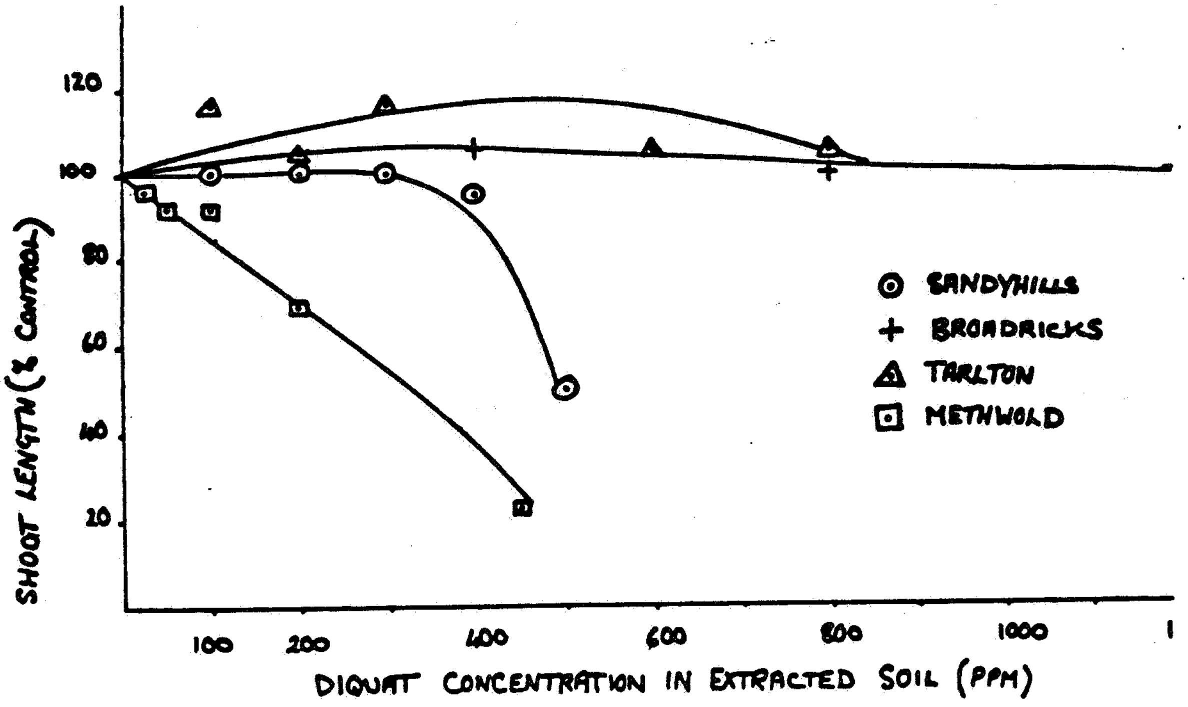

Figure 1.[a] Wheat bioassay (shoot length) of solutions from soils treated with diquat dibromide (Experiment 1).

a Graph presented as in hardcopy.

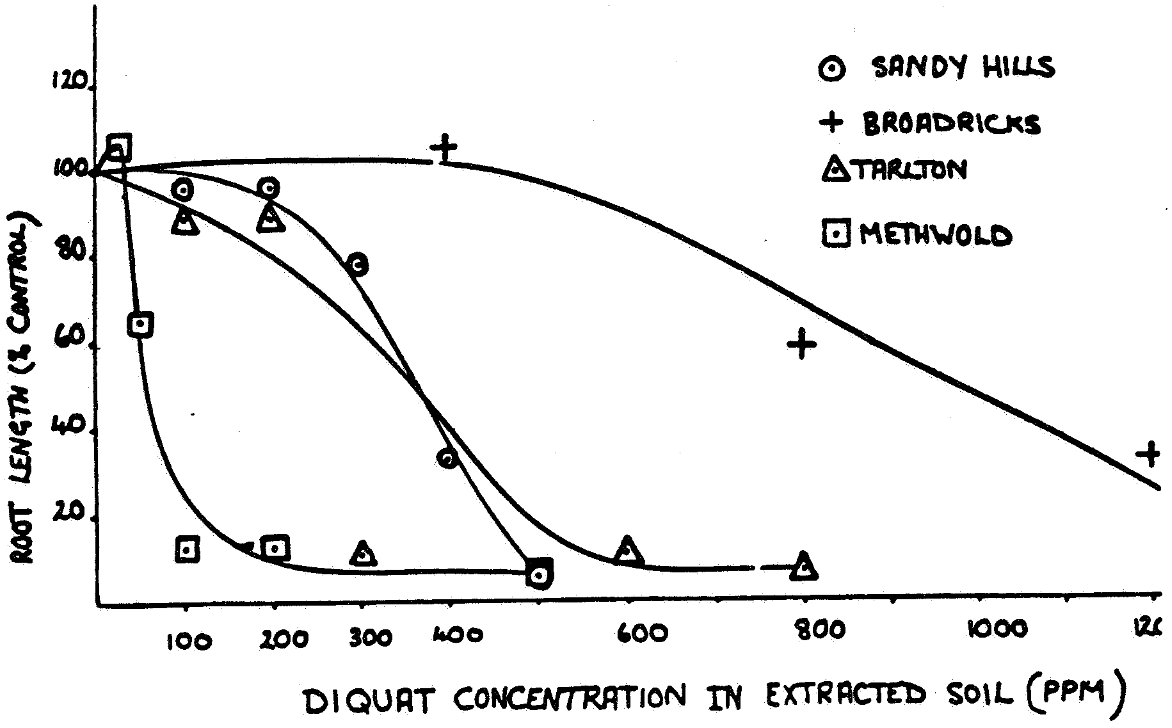

Figure 2.[a] Wheat bioassay (root length) of solutions from soils treated with diquat dibromide (Experiment 1).

[a] Graph presented as in hardcopy.

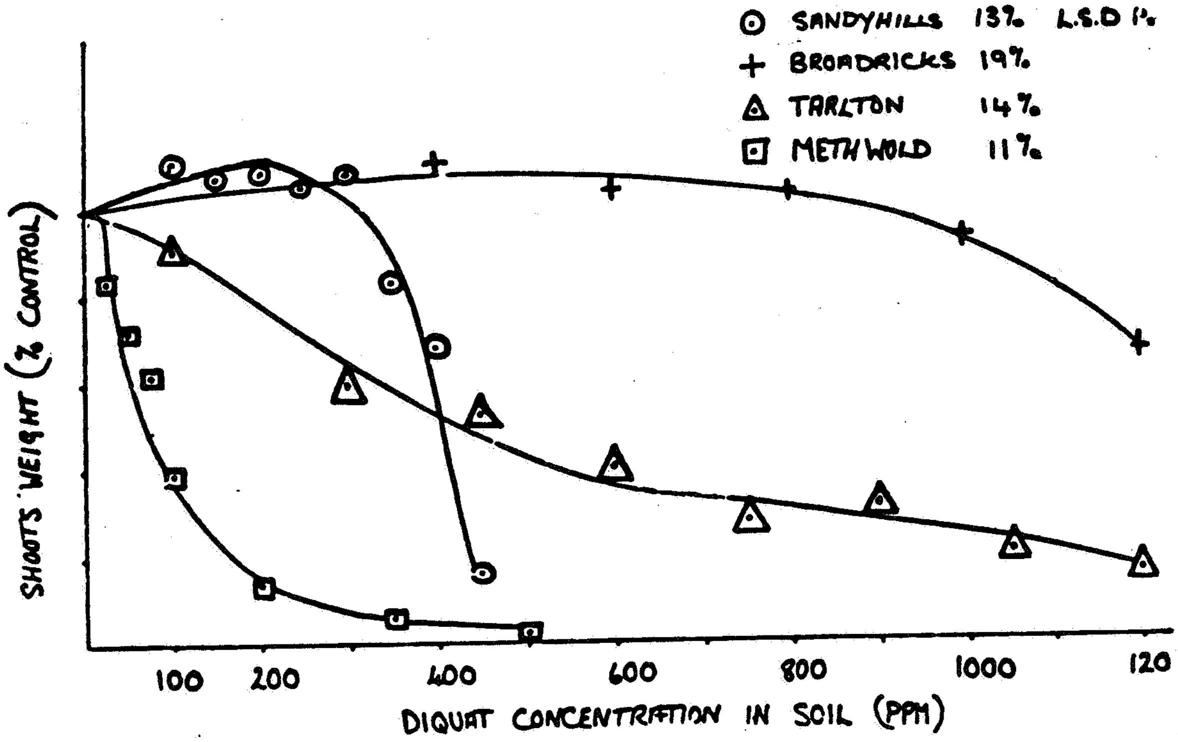

Figure 3.^{a} Wheat bioassay (shoot weight) of soils treated with diquat dibromide (Experiment 2).

a Graph presented as in hardcopy.

Table 1. Soil characteristics.

Soil	Sand	Silt	Clay	Organic matter	pH
	%				
Sandy Hills sandy loam	79	10	11	1.7	6.7
Broadrick's sandy loam	65	18	17	1.9	5.8
Tarlton loam	31	48	21	4.8	7.8
Methwold fen peat	--[a]	--	--	42.3	7.3

[a] Not reported.

Table 2. The concentrations of diquat dibromide phytotoxic residues (ppm)[a] in soils treated with diquat dibromide at 100 to 1200 ppm (Experiment 2).

Soil	Bioassay	Diquat residues (ppm)
Sandy Hills	Wheat 1st crop	350
Sandy Hills	Wheat 2nd crop	470
Sandy Hills	Wheat 2nd crop	470
Sandy Hills	Wheat 2nd crop	400
Broadrick's	Wheat 1st crop	1100
Broadrick's	Radish 2nd crop	1100
Tarlton	Wheat 1st crop	175
Methwold	Wheat 1st crop	20
Methwold	Wheat 2nd crop	50
Methwold	Wheat 3rd crop	75
Methwold	Wheat 3rd crop	50
Sandy Hills	*Lemna*	500
Sandy Hills	*Lemna* with $CaCl_2$	500

[a] The lowest concentration (ppm cation) to significantly ($P = 0.05$) affect plant growth.

(TDR03B) DATA EVALUATION RECORD PAGE 1 OF 11

CASE GS0288 DIQUAT DIBROMIDE STUDY 2 PM --

CHEM 032201 Diquat Dibromide

BRANCH EFB DISC --

FORMULATION 90 - FORMULATION NOT IDENTIFIED

FICHE/MASTER ID 00052389 CONTENT CAT 01
Wilkinson, W. 1980. Paraquat and diquat: long-term high-rate trial, Frensham, U.K. 1. Management of site, effects on crops and weeds and residues in crops: Report Series RJ 0013 B. Unpublished study received June 4, 1980 under 239-2186; prepared by ICI, submitted by Chevron Chemical Co., Richmond, CA; CDL:242577-A.

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Gowman, M.A., D. Riley, and S.E. Newby. 1980. Paraquat and diquat: long-term high-rate trial, Frensham, U.K. 2. Persistence and Movement in soil, and glasshouse bioassays: Report Series RJ 0014 B. Unpublished study received June 4, 1980 under 239-2186; prepared by ICI, submitted by Chevron Chemical Co., Richmond, CA; CDL:242577-B.

SUBST. CLASS = S.

DIRECT RVW TIME = 12 (MH) START-DATE END DATE

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TITLE:
ORG:
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SIGNATURE: DATE:

Two hardcopies were reviewed for this study. One hardcopy (00052390) contains soil residue data, and the other hardcopy (00052389) contains barley and carrot residue data.

CONCLUSION:

Field Dissipation - Long Term

This study cannot be validated because the data are too variable and the analytical methods were not described in sufficient detail to accurately assess the dissipation of the test substance from soil. In addition, this study does not fulfill EPA Data Requirements for Registering Pesticides because the test substance was not a typical end-use product, the soil was not from the U.S., more than one pesticide was applied to the soil, no pre- or immediate posttreatment samples were taken, degradates were not identied, complete field test data were not provided, and a nonspecific analytical method was used.

MATERIALS AND METHODS:

Plots (40 x 5 m) of Frensham loamy sand soil (83% sand, 8% silt, 9% clay, 2.0% organic matter, CEC 5.7 meq/100 g, pH 6.6) near Surrey, England which were plowed, rolled, harrowed twice and rolled again were treated with diquat dibromide (27.5% pure, Chevron Chemical Co.) at 0, 90, 198, and 720 kg cation/ha and soil incorporated to a depth of 15 cm (deep), and at 0, 15, 33, and 120 kg cation/ha and soil incorporated to a depth of 2.5 cm (shallow). The plots were treated in November, 1971. Barley (Hordeum vulgare) was drilled into the plots in the spring of 1972, 1973, and 1975-1977 at 1.25 cwt/A. The plots were fertilized normally and treated with selective hormone weed killers, and after each harvest an overall stubble cleaning application of Gramoxone W (20% paraquat ion) at 1.5-3.0 pt/A was applied for a total of 8.9 kg paraquat/ha. In 1974 in order to control couch grass (Asropyron repens) the plots were rototvated to a depth of 15 cm after which the evaluation of the shallow incorporated plots (2.5 cm) was discontinued. Soil samples (20-25) were taken from the deep incorporated plots each spring and autumn during 1972-1978 (first sample taken 19 weeks posttreatment) to a depth of 0-7.5 and 7.5-15 cm or 0-5, 5-10, and 10-15 cm. Soil samples from the shallow incorporated plots were taken to a depth of 5 cm. On several occasions (unspecified) samples were taken to a depth of 15-22.5 cm and 22.5-30 cm to determine the vertical movement of diquat dibromide in the soil. At 80, 104, ~300 weeks posttreatment soil samples were taken to a depth of 15 cm in control plots 0.3 and 2.5 cm, 1, 2, and 3 m, and 15 and 30 cm, respectively, outside the treated plots to determine any lateral movement of diquat dibromide. At the end of the experiment (March 1979) additional soil samples were taken from the control plots. Samples from the same plots were combined, air-dried, and weighed.

Collected soil samples were placed in polythene [sic] bags and air-dried within 1 month of sampling. Samples taken up to May 15, 1973 were stored at room temperature; those taken between 1973-1977 were stored at 5 C; and those taken after 1978 were stored at -15 C. Most samples were analyzed within 6 months of collection. The air-dried samples were ground, sieved (1 mm) and 25 g subsamples were extracted with 12 N sulfuric acid. The extracts were cleaned up on a cation exchange resin, reduced with alkaline dithionite and analyzed colormetically (method referenced, not further described: ICI Plant Protection Division Report PPRAM-6, 6 Dec. 1972. Determination of residues of diquat in soil:spectrophotometric method). For samples fortified with diquat dibromide at 200, 80, and 4 µg/g the recovery values were 86, 94, and 86%, respectively.

Soil samples taken at 2-3 days and 11, 19, 50, 108, and 130 weeks posttreatment from the deeply incorporated (15 cm) plots were bioassayed by placing 150 g of soil in a pot (7.5 cm diameter), planting 10 wheat seeds, and covering the seeds with 50 g of soil. The plots were placed on a sand-bed in a glasshouse, the seedlings harvested after 2-3 weeks, and shoot dry weight and root length were measured in comparison to controls. In addition, soil (~1 kg) sampled at 25, 50, 80, and 130 weeks posttreatment were either mixed moist (5 minutes) or air-dried overnight then rewetted and mixed prior to the wheat bioassay.

Before the main harvest, barley was harvested from each plot (40-0.5 m rows), and stored at -15 C until analysis. The grain and straw were analyzed for diquat dibromide by a referenced (not provided) method (PPRAMS 5. Plant Protection, Residue analytical method No. 5. Determination of residues of diquat in crops and animal tissues (Spectrophotometric). Standard Operating Procedure 02/005/01).

In June, 1973 soil samples (100 mm deep) were taken from the deeply incorporated plots, mixed, and used to fill earthenware pots (290 mm i.d. and 380 mm deep). About 20 carrot seeds (<u>Daucus carota</u>) were sown (10 mm deep) in each pot and watered daily. Plants were thinned to ~15/pot, fertilized, and treated with 250 mg ai/l of pirimicarb (not characterized) for a aphid infestation. Carrots were harvested 118 days postplant and analyzed for diquat dibromide residues by a referenced (not provided) method (PPRAM 1. Plant Protection, Residue analytical method No. 1. Determination of residues of paraquat in crops. (Spectrophotometric). Standard Operating Procedures 02/001/01). The soil samples were analyzed for diquat dibromide as described above.

REPORTED RESULTS:

Diquat dibromide residues in loamy sand soil did not substantially dissipate over a period of 7 years when soil incorporated to a depth of 2.5 or 15 cm (Tables 1 and 2). Diquat dibromide residues moved laterally from the plots treated at 720 kg cation/ha with maximum recorded movement occurring at a depth of 0-7.5 cm ~6 years after soil incorporation to a depth of 15 cm (Table 3). Wheat shoot dry weight and root length were adversely affected by the presence of diquat dibromide phytotoxic residues, especially at the highest rate (720 kg cation/ha) of application (Table 4). Mixing or drying and mixing the soil samples prior to the wheat bioassay produced various differences in shoot and root growth (Table 5). Diquat dibromide residues in the straw and grain of barley grown on the treated plots were negligible regardless of the application rate or depth of soil incorporation (Table 6). Diquat dibromide residues in carrots grown in diquat treated soil accumulated to a maximum of 0.02 μg/g (Table 7). Carrots did not grow in soil treated with diquat at 720 kg cation/ha.

DISCUSSION:

1. Diquat dibromide residues in soil from treated plots were highly variable, therefore, it is not possible to accurately assess the dissipation of diquat dibromide from soil.

2. The analytical methods for determining the amount of diquat dibromide in soil were referenced but not completely described; the analytical methods for diquat dibromide in barley, wheat, and carrots were referenced but not provided.

3. More than one pesticide was applied to the plots which may have affected the dissipation of the test substance. In addition, it is not clear whether the colorimetric method used for soil analysis could adequately distinguish diquat dibromide from paraquat.

4. The test substance was reported as unformulated (concentrate, without surfactant) but only 27.5% pure, and therefore not a typical end-use product.

5. No pre- or immediate posttreatment samples were taken to confirm the application rates.

6. Complete field test data, such as amount of rainfall or irrigation, depth to the water table, slope of the plots, and soil and air temperatures, were not reported.

7. Degradates were not identified.

8. No explanation was offered for the paraquat residues found in barley grain and straw.

9. The soils used were foreign with no direct correlation to U.S. soils.

10. Deep soil samples taken between 2 days and 130 weeks were analyzed by a nonspecific bioassay technique that cannot determine action of parent diquat from the action of diquat degradates or other herbicides.

Table 1. Diquat dibromide residues (μg/g) in plots of loamy sand soil treated with diquat dibromide at 90, 198, and 720 kg cation/ha and soil incorporated to a depth of 15 cm.

Application rate (kg cation/ha)	Sampling depth (cm)	Sampling interval (weeks)													
		19	50	80	105	130	159	185	211	240	264	289	315	341	369
90	0-5	--	--	--	--	--	--	--	38	--	--	--	44	--	--
	0-7.5	47^{a}	55	50	--	51	50	37	--	43	37	41	--	34	32
	5-10	--	--	--	--	--	--	--	40	--	--	--	41	--	--
	7.5-15	51^{a}	60	32	24^{b}	17	37	22	--	41	35	41	--	23	30
	10-15	--	--	--	--	--	--	--	11	--	--	--	37	--	--
	15-22.5	1.9	--	--	--	--	--	--	--	--	--	--	--	--	--
198	0-5	--	--	--	--	--	--	--	86	--	--	--	80	--	--
	0-7.5	100	130	108	--	124	129	88	--	80	68	70	--	70	58
	5-10	--	--	--	--	--	--	--	99	--	--	--	93	--	--
	7.5-15	128	110	80	--	41	87^{b}	51	--	78	68	63	--	56	47
	10-15	--	--	--	--	--	--	--	24	--	--	--	80	--	--
	15-22.5	5.9	--	--	--	--	--	3.8	21	--	--	--	--	--	--
	22.5-30	--	--	--	--	--	--	2.6	3.0	--	--	--	--	--	--
720	0-5	--	--	--	--	--	--	--	435	--	--	--	274	--	--
	0-7.5	280	557	400	--	435	320	347	--	275	237	277	--	226	235
	5-10	--	--	--	--	--	--	--	348	--	--	--	272	--	--
	7.5-15	320	407	280	186^{b}	122	304	237	--	200	268	239	--	143	190
	10-15	--	--	--	--	--	--	--	242	--	--	--	212	--	--
	15-22.5	31	--	--	17^{b}	--	--	12	70	--	--	--	--	--	--
	22.5-30	--	--	--	2.4^{b}	--	--	8.6	2.1	--	--	--	--	--	--

[a] Mean of 2 samples.

[b] Reanalyzed in 1978 after prolonged storage.

Table 2. Diquat dibromide residues (μg/g and kg/ha) in plots of loamy sand soil treated with diquat dibromide at 15, 33, and 120 kg cation/ha, soil incorporated to a depth of 2.5 cm, and sampled to a depth of 5 cm.

Application rate (kg cation/ha)	Sampling interval (weeks) 19		50		80		105		130	
	(μg/g)	(kg/ha)	(μg/g)	(kg/ha)	(μg/g)	(kg/ha)	(μg/g)	(kg/ha)	(μg/g)	(kg/ha)
15	22	12.8	18	9.9	17	8.7	11	6.6	23	12.4
33	48	26.7	--	--	30	15.1	25	12.9	46	24.5
120	163	88.9	--	--	182	99.2	172	95.7	146	79.6

Table 3. Diquat dibromide residues (μg/g) in control plots adjacent to plots of loamy sand soil treated with diquat dibromide at 720 kg cation/ha and soil incorporated to a depth 15 cm.

Sampling depth (cm)	Diquat residues (μg/g)			
	Treated plot	Control plot Distance from treated plot		
		0.3 m		2.5 m[a]
0-7.5	400	5.0		1.2
7.5-15	280	1.5		0.5
		1 m	2 m	3 m[b]
0-15	--	0.9	0.6	0.2
		15 cm		30 cm[c]
0-7.5	277	32.0		22.6
7.5-15	239	16.5		16.5

[a] Soil samples taken May 15, 1973.

[b] Soil samples taken November 6, 1973.

[c] Soil samples taken June 3, 1977.

Table 4. Shoot dry weights and root lengths (% of control) of wheat grown in loamy sand soil from the top 15 cm of plots treated with diquat dibromide at 90, 198, and 720 kg cation/ha and soil incorporated to a depth of 15 cm.

Application rate (kg cation/ha)	Sampling interval						
	(Days)	(Weeks)					
	2-3	11	19	50	80	108	130
			Shoot dry weights (% of control)				
90	75[a]	97	65[a]	93	53	98	85
198	74[a]	87	68[b]	85	126	93	77[b]
720	7[a]	12[a]	6[a]	9[a]	18[a]	11[a]	6[a]
			Root lengths (% of control)				
90	25	25	25	72[a]	42[a]	105	100
198	10	15	10-15	20[a]	73[b]	95	41[a]
720	0	0	0	3[a]	3[a]	5[a]	0[a]

[a] Significantly different from the untreated control at P = 0.01.

[b] Significantly different from the untreated control at P = 0.05.

Table 5. Mean shoot dry weight (g) and root length (cm) of wheat grown in samples of soil which were mixed, unmixed, or dried and mixed, taken from plots of loamy sand soil treated with diquat dibromide at 90, 198, and 720 kg cation/ha.

Application rate (kg cation/ha)	Treatment	Sampling interval (weeks)			
		50	80	108	130
		Shoot dry weight (g)			
90	Unmixed	--	53[a]	85	94
	Mixed	--	150[a]	110	75[a]
	Dried and mixed	--	--	--	--
198	Unmixed	0.30[a](130)[b]	126	81	81
	Mixed	0.25 (109)	126	97	94
	Dried and mixed	0.23 (100)	--	--	--
720	Unmixed	0.00[a](0)	18[a]	10[a]	6[a]
	Mixed	0.01[a](4)	33[a]	102	12[a]
	Dried and mixed	0.01[a](4)	--	--	--
		Root length (cm)			
90	Unmixed	--	44[a]	105	94
	Mixed	--	94	100	101
	Dried and mixed	--	--	--	--
198	Unmixed	4.5[a](21)	75	95	39
	Mixed	2.0[a](10)	86	95	78
	Dried and mixed	7.0[a](33)	--	--	--
720	Unmixed	0.0[a](0)	3	5[a]	0[a]
	Mixed	0.0[a](0)	3	13[a]	0[a]
	Dried and mixed	0.3[a](1)	--	--	--

[a] Significantly different from untreated control at $P = 0.05$.

[b] Figures in parenthesis are percent of untreated controls.

Table 6. Diquat dibromide residues (μg/g) in barley straw and grain grown on plots of loamy sand soil treated with diquat dibromide at 0, 90, 198, and 720 kg cation/ha or at 0, 15, 33, and 120 kg cation/ha and soil incorporated to a depth of 15 or 2.5 cm, respectively.

Application rate (kg cation/ha)	Depth of incorporation (cm)	Sampling interval (year)[a]					
		1972		1973	1975	1976	1977
		Straw[bc]	Grain[de]	Grain[c]	Grain[f]	Grain[f]	Grain[g]
0	15	<0.1[h]	<0.01[i]	<0.1	<0.04	<0.04	<0.05
90	15	<0.1	<0.01[i]	<0.1	<0.04	<0.04	<0.05
198	15	<0.1	<0.01[i]	<0.1	<0.04	<0.04	<0.05
720	15	1.2	0.02	0.2	<0.04	<0.04	<0.05
0	2.5	<0.1	<0.01[i]	<0.1	--[k]	--	--
15	2.5	NA[j]	<0.01[i]	<0.1	--	--	--
33	2.5	NA	0.02	<0.1	--	--	--
120	2.5	<0.1	<0.01[i]	<0.1	--	--	--

[a] Samples taken just prior to general harvest.

[b] Oven dry weight.

[c] Limit of detection was 0.1 μg/g.

[d] Fresh (air-dried) weight.

[e] Limit of detection was 0.01 μg/g.

[f] Limit of detection was 0.04 μg/g.

[g] Limit of detection was 0.05 μg/g.

[h] Sample contained 0.11 μg/g of paraquat.

[i] Sample contained 0.01-0.03 μg/g of paraquat.

[j] Not analyzed.

[k] Test discontinued; no samples taken.

Table 7. Diquat dibromide residues (μg/g) in soil and in carrots grown in soil treated with diquat dibromide at 90, 198, and 720 kg cation/ha taken from plots cultivated to a depth of 15 cm.

Application rate (kg cation/ha)	Diquat residues (μg/g)	
	Soil	Carrots[a]
90	48	0.02
198	103	0.01
720	453	No crop[b]

[a] Limit of detection in carrots was 0.01 μg/g.

[b] Carrots did not grow in soil treated at the highest rate.

(TDR03B) DATA EVALUATION RECORD

CASE GS0288 DIQUAT DIBROMIDE STUDY 3 PM --

CHEM 032201 Diquat Dibromide

BRANCH EFB DISC --

FORMULATION 90 - FORMULATION NOT IDENTIFIED

FICHE/MASTER ID 00068232 CONTENT CAT 01
Yeo, R.R. 1967. Dissipation of diquat and paraquat and effects on aquatic weeds and fish. Weeds 15:42-46. Also In unpublished submission received Aug. 22, 1977 under 239-1663; submitted by Chevron Chemical Co, Richmond, CA; CDL: 231431-R.

SUBST. CLASS = S.

DIRECT RVW TIME = 9 (MH) START-DATE END DATE

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CONCLUSIONS:

Field Dissipation - Aquatic and Aquatic Impact

1. The portion of this study pertaining to the plastic pools is scientifically valid (Experiment 2). However, the portion of this study pertaining to the natural reservoirs (Experiment 1) is scientifically invalid because the water flow into and out of the sites was not characterized.

2. Diquat (test substance uncharacterized) at 500, 1000, and 4000 ppbw dissipated in the water of plastic pools (4 ft^2 x 2 ft deep) containing soil with ~20, 30, and 600-900 ppbw detected 12 days posttreatment. Different levels of total water hardness did not affect the dissipation rate of diquat from water.

3. This study does not fulfill EPA Data Requirements for Registering Pesticides because the test substance was uncharacterized, the soil and water were not completely characterized, field test data were incomplete, there was no pretreatment sampling, soil samples were not taken, the pattern of formation and decline of degradates was not addressed, the sampling procedures were not described, and a nonspecific analytical method was used.

MATERIALS AND METHODS:

Experiment 1

Reservoirs (not characterized) near Davis, California were treated with diquat (test substance uncharacterized, source unspecified) at 125, 250, 500, and 1000 ppbw by injection into the water from a moving boat. Water samples (1 gal) were taken at 0.5 hours and 4, 8, and 12 days after treatment, and stored frozen until analysis.

The amount of diquat present in the samples was determined colorimetrically with a spectrophotometer at wavelength of 370 mμ as in a referenced (not provided) method (Chevron Chemical Co., Ortho Division. 1961. Analysis of diquat, residue method RM 5A, Richmond, CA). Samples from the 1000 ppbw treatment were analyzed directly, whereas samples from treatments at lower rates were concentrated in exchange columns using a cation resin. The adsorbed diquat was eluted with sodium chloride, and sodium dithionite was added to the eluate and the color density determined. Recovery values were ~90%.

Experiment 2

In a related experiment, 2 inches of clay loam soil (soil not further characterized) was placed in plastic pools (4 ft^2 x 2 ft deep) and flooded with 180 gal of water (water not characterized). Aquatic plants, fish, and 1 liter of natural pond water was added to the pools to simulate natural conditions. Increments (unspecified) of calcium chloride were added to some of the pools to achieve three levels of total water hardness. Total hardness and pH were measured at the beginning and end (30 days) of the experiment. The pools were treated with diquat (test substance uncharacterized, source unspecified) at 0, 500, 1000, and 4000 ppbw at each level of water hardness with three replicates of each treatment.

Water samples (1 gal) were taken at 0.5 hours, and 4, 8, and 12 days posttreatment and analyzed as in Experiment 1.

REPORTED RESULTS:

Ranges of environmental factors measured in the treated reservoirs are shown in Table 1. In the treated pools the pH averaged ~8.5, and total hardness ranged from 120-122, 139-161, and 159-191 ppmv for the low, medium, and high levels, respectively, at the beginning of the study.

Experiment 1

In the reservoirs, diquat at 125, 250, 500, and 1000 ppbw dissipated to 84, 4, 24, and 22% of applied, respectively, 0.5 hours after application (Table 2). In all treatments of 1000 ppbw or less diquat dissipated to <60, <20, and <9 ppbw after 4, 8, and 12 days, respectively (Figure 1).

Experiment 2

In the pools, the rate of diquat dissipation was slower than in the reservoirs, with 600-900 ppbw detected 12 days after the application of diquat at 4000 ppbw (Figure 2). However, 12 days after the application of diquat at 500 and 1000 ppbw, ~20 and ~30 ppbw of diquat were detected. Different levels of total water hardness did not affect the dissipation.

DISCUSSION:

General

1. The test substance was uncharacterized.
2. Complete soil characteristics, such as textural analysis, organic matter content, CEC, and pH, were not provided.
3. There was no pretreatment sampling.
4. Soil samples were not taken.
5. The pattern of formation and decline of degradates was not addressed.
6. The sampling procedures were not described, and a nonspecific analytical method was used.

Experiment 1

1. The flow of the water into and out of the reservoirs was not characterized, therefore, it could not be determined whether diquat dissipated within the reservoirs or was transported out of the sites.
2. The reservoirs were not described.

Experiment 2

1. The water in the pools was not characterized.

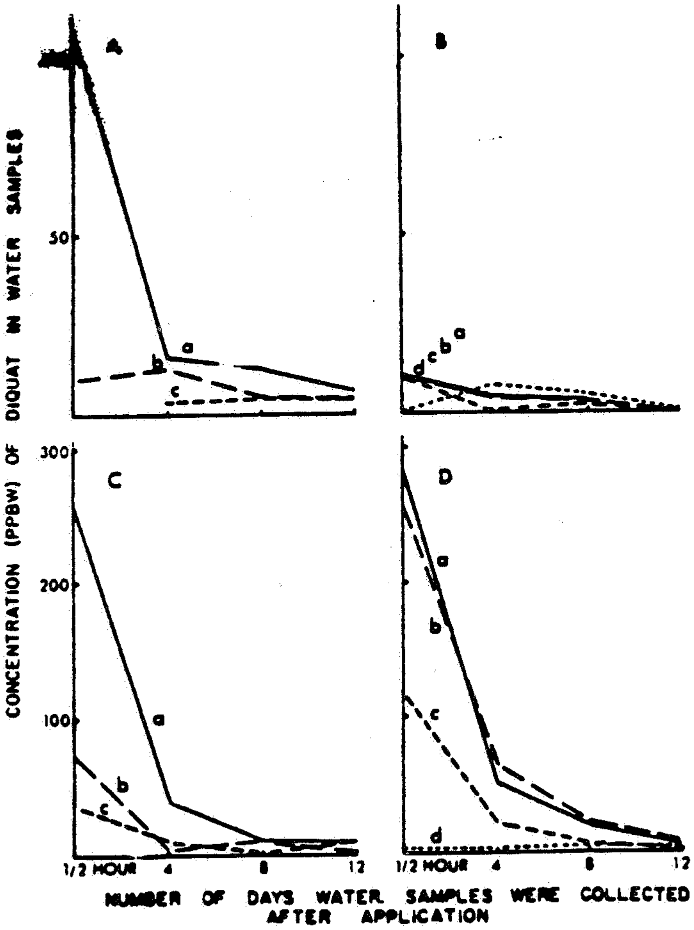

Figure 1.[a] Dissipation of the following concentrations of diquat from reserviors: A. 125 ppbw; B. 750 ppbw; C. 500 ppbw; and D. 1000 ppbw. Curves a, b, c, and d are for different reserviors treated with each concentration.

[a] Graphs presented as in hardcopy.

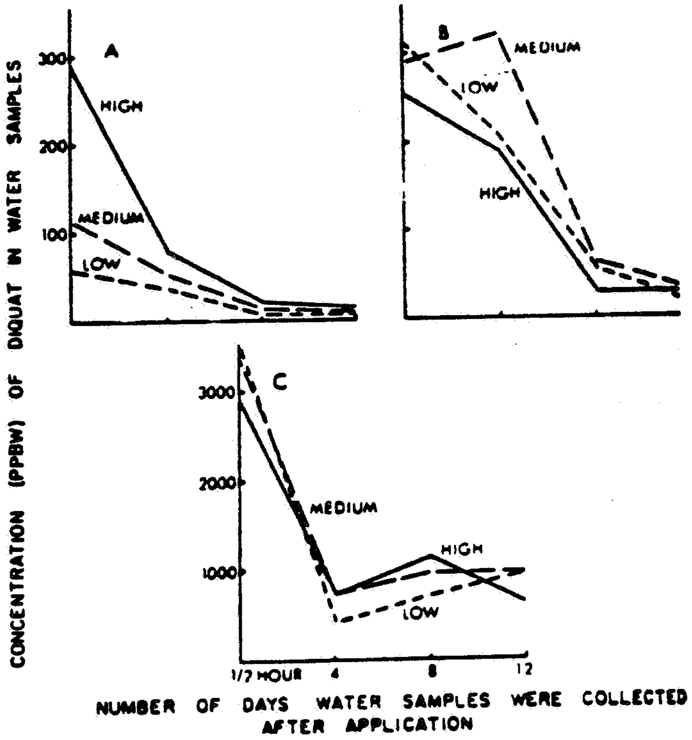

Figure 2.[a] Dissipation of the following concentrations of diquat from pools containing waters with low, medium, and high levels of hardness: A. 500 ppbw; B. 1000 ppbw; and C. 4000 ppbw.

[a] Graphs presented as in hardcopy.

Table 1. Ranges of environmental factors in reservoirs treated with diquat at 125, 250, 500, and 1000 ppbw.

Environmental factor	Application rate of diquat (ppbw)			
	125	250	500	1000
Turbidity[a]	2	2-5	1-2	2-5
Water temperature (F)	69-70	66	60-67	63-68
Calcium hardness (ppmw)	21-36	68	90-168	51-168
Total hardness (ppmv)	40-90	240	110-240	240-359
Total alkalinity	44-104	240	100-240	240-308
pH	7.6-9.1	7.6	7.6-7.8	7.6-9.0
Average weed density[a]	3	4	4	5

0 Values represent visual estimates of turbidity and weed growth: 0 and 5 denote no turbidity or growth and extreme turbidity or dense growth, respectively.

Table 2. Diquat (% of applied) in water 0.5 hours after application from reservoirs and pools treated with diquat at 125, 250, 500, 1000, and 4000 ppbw.

Application rate (ppbw)	Reservoirs	Pools
125	84	--
250	4	--
500	24	30
1000	22	28
4000	--	79

(TDR03B) DATA EVALUATION RECORD PAGE 1 OF 4

CASE GS0288 DIQUAT DIBROMIDE STUDY 4 PM --

CHEM 032201 Diquat Dibromide

BRANCH EFB DISC --

FORMULATION 90 - FORMULATION NOT IDENTIFIED

FICHE/MASTER ID 00100609 CONTENT CAT 01
Schreck, C., R. Corning, and C. Berry, et al. 1974. Aquatic plant control using herbicides in a large potable water supply reservoir. Annual rept., July 1, 1973--June 30, 1974: Contract No. DACW65-74-C-0013. Virginia Polytechnic Institute and State Univ., Dept. of Fisheries and Wildlife Sciences for U.S. Dept. of the Army, Corps of Engineers; unpublished study; CDL:247354-B.

SUBST. CLASS = S.

DIRECT RVW TIME = 2 1/2 (MH) START-DATE END DATE

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CONCLUSIONS:

Field Dissipation - Aquatic and Aquatic Impact

1. This study is scientifically valid.

2. Diquat dibromide (test substance uncharacterized) at 0.23 ppm dissipated in reservoir water to nondetectable levels (<0.01 ppm) in 10-15 days.

3. This study does not fulfill EPA Data Requirements for Registering Pesticides because more than one pesticides was applied; the test substance was uncharacterized; the water, soil, and sediment were uncharacterized; the soil or sediment was not sampled; complete field test data were not reported; the pattern of formation and decline of degradates was not addressed; and a nonspecific analytical method was used.

MATERIALS AND METHODS:

Two areas in the Chickahominy Reservoir in Virginia designated as FWQ (lotic, 28 A, ~2 cm-4 m deep, flow rate <0.05 feet/second) and SWQ (lentic, 35 A, ~2 cm-2.5 m deep, flow rate nil) both of which had about 45-50% open water were treated (by airboat) with a mixture of diquat dibromide (test substance uncharacterized, Chevron Chemical Co.) at 0.23 ppm and endothal (Aquathol K, purity unspecified, Pennwalt Corp.) at 0.17 ppm. Triplicate water samples (volume and sampling method unspecified) were taken in glass jars pretreatment, at 4, 12, 20, 28, and 40 hours, daily for 1 month, and monthly thereafter.

The water samples were fixed with sulfuric acid (to pH 2), and stored frozen until analysis. The samples were thawed, cleaned up on a cation exchange column, and eluted from the column with saturated ammonium chloride. The eluate was analyzed colorimetrically after adding dithionite as an indicator to quantify diquat dibromide. Recovery values were ~80% and the detection limit was 0.01 ppm. The complete analytical procedure was referenced (Method PM-5, Chevron Chemical Co. 1970.) but not provided.

REPORTED RESULTS:

Diquat dibromide dissipated from the reservoir water to nondetectable levels by 15 and 9 days in the lotic and lentic sites, respectively (Table 1, Figure 1).

DISCUSSION:

1. More than one pesticide was applied to the reservoir water which may have affected the dissipation of diquat dibromide in water.
2. The test substance was uncharacterized.
3. The water, soil, and sediment were not characterized.
4. The soil/sediment was not sampled.
5. Complete field test data, such as sampling technique and sample volume, were not reported.
6. The pattern of formation and decline of degradates was not addressed.
7. The detection limit was reported as 0.01 ppm but the data are reported (Table 1) at 0.00 ppm.

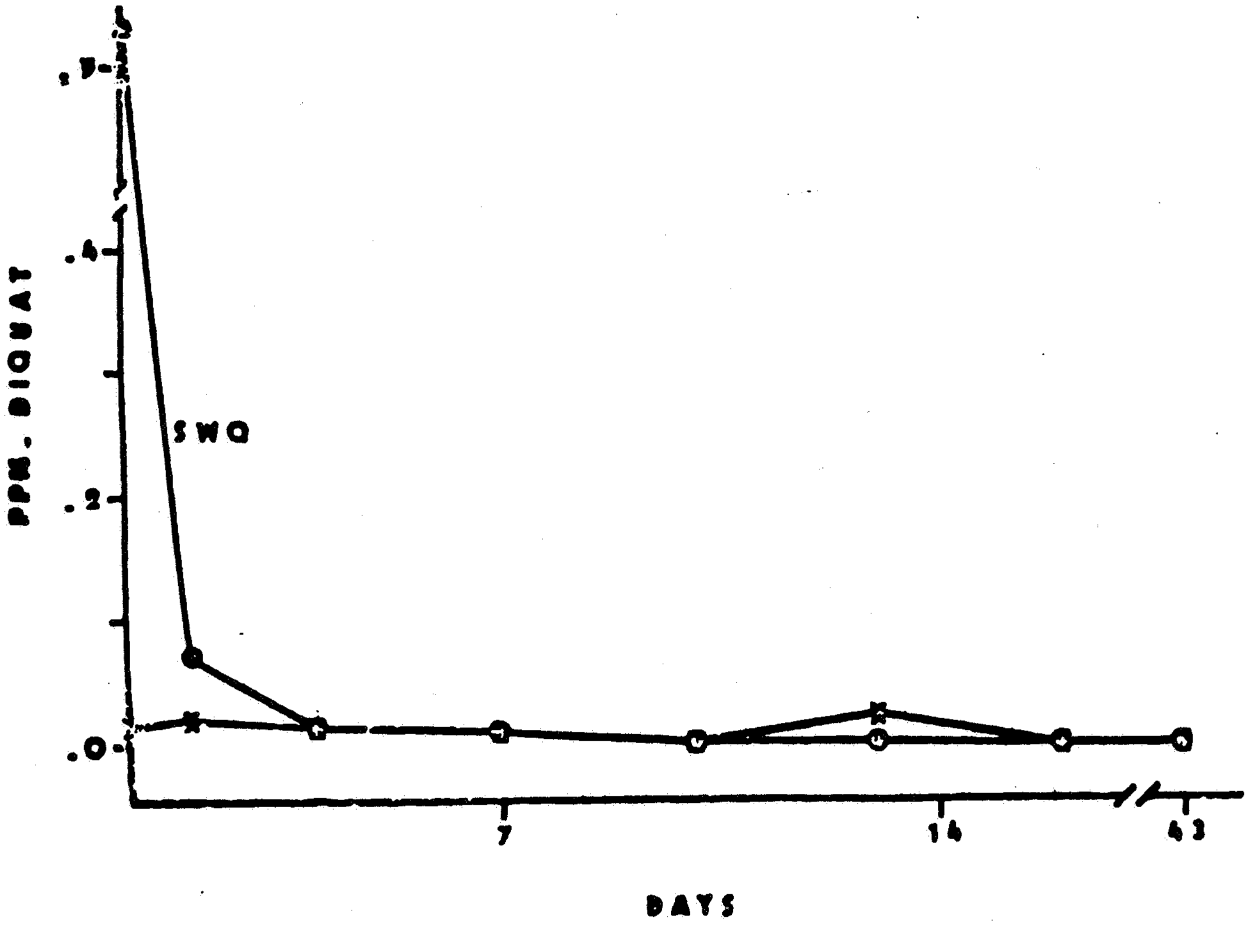

Figure 1.[a] The dissipation of diquat dibromide applied at 0.23 ppm in water at two sites in a reservoir.

[a] Graph presented as in hardcopy.

Table 1. Diquat dibromide in reservoir water treated with a mixture of diquat dibromide at 0.23 ppm plus endothal at 0.17 ppm.

Sampling interval	FWQ[a]	SWQ[b]
Pretreatment	0.01	0.00
4 hours	0.00[c]	0.73
12	0.03	0.11
20	0.01	0.07
28	0.00	0.00
40	0.02	0.00
3 days	0.02	0.01
4	0.00	0.02
6[d]	0.01	0.01
9	0.00	0.00
12	0.02	0.00
15	0.00	0.00
18	0.00	0.02
24	0.00	0.00
34	0.00	0.00
43	0.00	0.00

[a] Lotic site ~28 A.

[b] Lentic site ~35 A.

[c] Detection limit was 0.01 ppm.

[d] Each value for 6-43 days represents the average of 3 days (e.g., the 6th day represents an average of values compiled over the 5th, 6th, and 7th days).

(TDR03B) DATA EVALUATION RECORD PAGE 1 OF 3

CASE GS0288 DIQUAT DIBROMIDE STUDY 5 PM --

CHEM 032201 Diquat Dibromide

BRANCH EFB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No MRID CONTENT CAT 01
Upton, B.P., P. Hendley, and M.W. Skidmore. 1985. Diquat: Hydrolytic stability in water at pH 5, 7, and 9. ICI Plant Protection Division, Jealotts' Hill Research Station, Bracknell, Berkshire, UK. Accession Nos. 259950, 259951.

SUBST. CLASS = S.

DIRECT RVW TIME = 3 (MH) START-DATE END DATE

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CONCLUSIONS:

Degradation - Hydrolysis

1. This study is scientifically valid.

2. $[^{14}C]$Diquat (100% pure, specific activity 0.122 GBq/mM) at ~55 mg cation/l was stable to hydrolysis in sterile, aqueous solutions buffered at pH 5 and 7 when incubated in the dark at 25 C for 30 days. At pH 9 $[^{14}C]$diquat degraded by ~10% over the 30 day incubation period.

3. This study fulfills EPA Data Requirements for Registering Pesticides by providing information on the hydrolysis of diquat at pH 5, 7, and 9.

MATERIALS AND METHODS:

Under sterile conditions, glass distilled water was buffered to pH 5 (0.1 M potassium hydrogen phthallate:0.05 M sodium hydroxide, 1:1), pH 7 (0.1 M potassium dihydrogen orthophosphate:0.1 M disodium hydrogen phosphate 1:19), and to pH 9 (0.1 M potassium chloride in 0.1 M boric acid:0.05 M sodium hydroxide, 1:1). The buffer solutions, placed in conical flasks, were treated with a stock solution containing ring-labeled [^{14}C]diquat dichloride (specific activity 0.398 GBq/mM, 100% pure, ICI Petrochemicals Division) and nonlabeled diquat dibromide (100% pure, ICI Petrochemicals Division) for a final average diquat concentration of ~55 mg cation/l and a specific activity of 0.122 GBq/mM. The flasks were tightly stoppered and incubated in a constant temperature, shaking water bath at 25 C in the dark. Samples were taken at 0, 2, 8, 16, and 30 days, and stored at -15 ± 5 C until analysis.

Duplicate samples were adjusted to a standard volume (unspecified) and analyzed directly by TLC by spotting on silica gel and cellulose plates and developing with 2 M hydrochloric acid:pentanol (97:3, v/v) and butan-1-ol:acetic acid:water (5:1:4, v/v/v), respectively. [^{14}C]-Diquat dibromide was visualized by spraying the plates with potassium iodoplatinate, and autoradiography. The average recovery values at all three pH levels were >90%

REPORTED RESULTS:

[^{14}C]Diquat was stable to hydrolysis in sterile, buffered aqueous solutions of pH 5 and 7, incubated at 25 C in the dark for 30 days (Table 1). At pH 9 [^{14}C]diquat degraded by ~10% over the 30 day incubation period. The pH of the test solutions was stable during the study.

DISCUSSION:

1. This study fulfills EPA Data Requirements for Registering Pesticides by providing information on the hydrolysis of diquat at pH 5, 7, and 9.

2. Degradates were not identified; however, this was not necessary because diquat was essentially stable to hydrolysis.

3. This study was conducted using [^{14}C]diquat dichloride mixed with unlabeled diquat dibromide. Use of [^{14}C]diquat dichloride was acceptable as bipyridyl herbicides are highly ionic and the active portion is the cationic diquat moiety. The radioactive ^{14}C-label was included on this cationic structure.

Table 1. [^{14}C]Diquat (% of applied [^{14}C]radioactivity)[a] in sterile, buffered, aqueous solution of pH 5, 7, and 9 incubated in the dark at 25 C for up to 30 days.

Sampling interval (days)	pH	Sample	[^{14}C]Diquat (% of applied)	Total [^{14}C]radioactivity (% of applied)
0	5	A	92.3	100.5
		B	93.5	100.25
	7	A	88.5	100.6
		B[b]	93.7	100.45
	9	A	86.45	100.7
		B	93.2	99.95
30	5	A	91.1	101.4
		B	91.8	99.95
	7	A	89.9	100.15
		B	88.5	102.95
	9	A	83.0	100.0
		B	72.6[c]	100.05
2	9	A	91.7	100.0
		B	91.3	101.15
8	9	A	88.85	99.95
16	9	A	83.0	99.8
		B[b]	88.2	100.0

[a] Mean values of results from the two TLC solvent systems.

[b] Samples run in only one TLC solvent system.

[c] This result was considered an anomoly because of a high percentage (16.85%) of [^{14}C]radioactivity remaining at the origin of the TLC plate. Therefore, the percent of [^{14}C]diquat in the pH 9 solution after 30 days has been taken from the results of Sample A.