

US EPA ARCHIVE DOCUMENT

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Date Out of EFGWB: FEB 21 1989

TO: Larry Schnaubelt
Product Manager 23, Acting
Registration Division (TS-767)

FROM: Paul Mastradone, Acting Section Chief *PM*
Environmental Chemistry Review Section #1
Environmental Fate and Groundwater Branch

THRU: Hank Jacoby, Chief (acting) *Hank Jacoby*
Environmental Fate and Groundwater Branch
Environmental Fate and Effects Division (TS-769C)

Attached please find the EFGWB review of:

Reg./File # : 239-¹/~~663~~

Chemical Name: Diquat Dibromide

Product Type : Herbicide

Product Name : Diquat Water Weed Killer

Company Name : Chevron Chemical Co./Ortho

Purpose : Remove reentry label restriction prohibiting swimming in treated areas within 14 days after treatment.

Date Received: 2/1/89

Action Code: 660

Date Completed: 2/21/89

EFGWB No. 90315

Total Reviewing Time (decimal days): 6.2

Deferrals to: Ecological Effects Branch, EFED
Science Integration & Policy Staff, EFED
XXX Non-Dietary Exposure Branch, HED
Dietary Exposure Branch
Toxicology Branch, HED

OFFICE OF PESTICIDE PROGRAMS DATA REVIEW RECORD

Confidential Business Information-Does Not Contain National Security Information(E.O. 12065)
 This form is to be used for individual studies and for submission of pesticide applications

1. PRODUCT NAME <i>Diquat Water Weed Killer</i>		CHEMICAL NAME <i>Diquat dibromide</i>		
2. IDENTIFYING NUMBER <i>239-1663</i>	3. RECORD NUMBER <i>239170</i>	4. ACTION CODE <i>660</i>	5. FRID/ACCESSION NUMBER <i>40927601</i> <i>40972302</i> <i>40418801</i> <i>40245101</i>	6. STUDY GUIDELINE OR NARRATIVE <i>162-4</i> <i>162-3</i> <i>161-2</i> <i>163-2</i>
7. REFERENCE NUMBER <i>100</i>	8. DATE RECEIVED (EPA) <i>11/19/89</i>	9. PRODUCT/REVIEW MANAGER/DCI <i>Mountbait</i>	10. PM/RM TEAM NUMBER <i>23</i>	11. DATE SENT TO (HED/EFED/RD/BEAD) <i>1/31/88</i>
12. PROJECTED RETURN DATE <i>3/31/89</i>	13. DATE RETURNED TO (RD/SRRD)	INSTRUCTIONS: <i>Please review data data submitted in response to requirements in the diquat registration standard. These items all pertain to data in the aquatic environment. Chevron has requested deletion of swimming restriction.</i>		

(THIS SECTION APPLIES TO REVIEW OF STUDIES ONLY)

14. CHECK APPLICABLE BOX:

ADVERSE 6(a)(2) DATA (405) GENERIC DATA (660) (REREGISTRATION) PRODUCT SPECIFIC DATA (655) (REREGISTRATION)

SPECIAL REVIEW DATA (870)

15. NUMBER OF INDIVIDUAL STUDIES SUBMITTED

16. HAVE ANY OF THE ABOVE STUDIES (in whole or in part) BEEN PREVIOUSLY SUBMITTED FOR REVIEW? (circle: yes or no) IF YES, PLEASE IDENTIFY THE STUDY(IES):

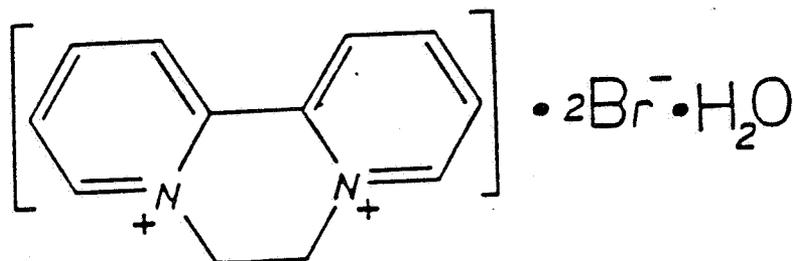
17. RELATED ACTIONS:

18. TO	TYPE OF REVIEW	19. REVIEWS ALSO SENT TO	20. DATA REVIEW CRITERIA
HED	SCIENCE ANALYSIS & COORD.	SAC _____ PC	A. Policy Note #31 <input type="checkbox"/> 1 = data which meet 6(a)(2) or meet 3(c)(2)(B) flagging criteria <input checked="" type="checkbox"/> 2 = data of particular concern from registration standard <input type="checkbox"/> 3 = data necessary to determine tiered testing requirements
	TOXICOLOGY/HFA	<input checked="" type="checkbox"/> TOX/HFA _____ PL	
	TOXICOLOGY/IR	TOX/IR _____	
	DIETARY EXPOSURE	DEB _____ EA	
	NON-DIETARY EXPOSURE	<input checked="" type="checkbox"/> NDE _____ AC	
EF ED	ECOLOGICAL EFFECTS	EEB _____ BA	<input checked="" type="checkbox"/> 2 = data of particular concern from registration standard
	<input checked="" type="checkbox"/> ENVIRONMENTAL FATE & GROUND H2O	EFGWB _____	
SRRD	SPECIAL REVIEW	SR _____	<input type="checkbox"/> 3 = data necessary to determine tiered testing requirements
	REREGISTRATION	RER _____	
	GENERIC CHEMICAL SUPPORT	GSC _____	
RD	INSECTICIDE-RODENTICIDE	IR _____	B. Section 18 <input type="checkbox"/> 1 = data in support of section 3 in lieu of section 18
	FUNGICIDE-HERBICIDE	FH _____	
	ANTIMICROBIAL	AM _____	
BEAD	PRODUCT CHEMISTRY		C. Inert Ingredients <input type="checkbox"/> 1 = data in support of continued use of List 1 inert
	PRECAUTIONARY LABELING		
	ECONOMIC ANALYSIS		
	ANALYTICAL CHEMISTRY		
	BIOLOGICAL ANALYSIS		

CONFIDENTIAL STATEMENT OF FORMULA (TRADE SECRETS) LABEL ATTACHED

White - Data Coordinator Pink - PM/RM/DCI
 Yellow - Data Review Section Green - Return with completed review
 Include original + two (2) copies with each submission

1. CHEMICAL: Common Name: Diquat Dibromide
Chemical Name: 6,7-Dihydrodipyrido (1,2-a: 2',1'-pyrazinediium dibromide
Trade Name: Ortho Diquat Water Weed Killer
Chemical Structure:



2. TEST MATERIAL: ^{14}C -ring-labelled analytical grade diquat
3. STUDY/ACTION TYPE: The registrant requests review of data to support removal of the label restriction prohibiting swimming in treated areas within 14 days after application.

4.0 STUDY IDENTIFICATION:

Johnson, J. J. 1988. Aerobic Aquatic Metabolism of Diquat. Laboratory Project Identification MEF-0073. Chevron Chemical Co., Ortho Agricultural Chemicals Division. Richmond, CA. MRID No. 409723-02

Johnson, J. J. 1988. Anaerobic Aquatic Metabolism of Diquat. Laboratory Project Identification No. MEF-0072. Chevron Chemical Co. Ortho Agricultural Chemical Division, Richmond, CA. MRID No. 409723-02.

Tegala, B. and M. W. Skidmore. 1987. Diquat: An Aqueous Photolysis Study. Laboratory Project Identification No. RJ 0613B. Chevron Chemical Co. Ortho Agricultural Chemicals Division. Richmond, CA. MRID No. 404188-01.

Pack, D. E.. 1987. Diquat Volatility - Laboratory Study. Laboratory Project Identification MEF-0045. Chevron Chemical Co.. Ortho Agricultural Chemicals Division, Richmond, CA. MRID No. 402451-01.

5.0 REVIEWED BY:

Clinton L. Fletcher
Chemist, EFGWB/EFED

Signature: 
Date: 2-21-89

6.0 APPROVED BY:

Paul J. Mastradone, Ph.D.
Acting Chief, Section 1, EFGWB/EFED

Signature: 
Date: []

7.0 CONCLUSION

The aqueous aerobic, anaerobic aquatic metabolism and aqueous photolysis studies are scientifically sound and are acceptable in satisfying the data requirements as required by Subdivision N of the Guidelines and the Reregistration Standard.

The Diquat Volatility-Laboratory Study has been satisfied. The DEB/HED (R. Perfetti) indicated that diquat dibromide is considered nonvolatile. According to the data included in this submission, at 25° C the vapor pressure of diquat is $<4 \times 10^{-9}$ mm Hg.

Thus, the following data requirements for diquat dibromide have been satisfied: Hydrolysis, Aqueous photolysis, Aerobic aquatic metabolism, Anaerobic aquatic metabolism, and laboratory volatility. All other Subdivision N Guideline data requirements remain outstanding.

Based on the data submitted, EFGWB considers diquat will be stable under aqueous aerobic and anaerobic conditions and also stable under aqueous photolytic conditions found in the environment. The data from the aqueous aerobic and anaerobic metabolism studies indicate that diquat quickly binds to the soil sediment. While the photolytic half-life for diquat was calculated to be 74 days, the fact that diquat binds to the soil sediment may exclude photodegradation as a means of diquat dissipating in the aquatic environment.

The 1,2,3,4-tetrahydro-1-oxopyridi (1,2-a) pyrazin-5-ium ion was the major photolytic degradation product. Four other photodegradates were found but not identified. Each accounted for less than 5% of the applied diquat. An unidentified degradation product was reported as found in minor amounts in the anaerobic aquatic metabolism study.

8.0 RECOMMENDATION

EFGWB/EFED recommends that the submitted aerobic aquatic and anaerobic aquatic metabolism and the aqueous photolysis be accepted as satisfying these data requirements in Subdivision N of the Guidelines.

EFGWB/EFED defers to NDEB/HED and SACB/HED regarding the registrant's request for deletion of the reentry label restriction.

9.0 BACKGROUND

The registrant, Chevron Chemical Co., has submitted a revised label requesting removal of the reentry label restriction prohibiting swimming in treated areas within 14 days after treatment. The RD submitted studies containing environmental fate data and physical chemical data supporting the registrant's request.

10.0 DISCUSSION OF INDIVIDUAL STUDIES:

See separate DATA EVALUATION RECORDS.

11. COMPLETION OF ONE-LINER:

Test results have been included.

12. CBI APPENDIX:

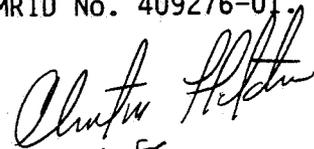
There is no CBI in this submission.

DATA EVALUATION RECORD

STUDY IDENTIFICATION: Johnson, J.J.. 1988. Aerobic Aquatic Metabolism of Diquat. Laboratory Project Identification MEF-0073. Chevron Chemical Co., Ortho Agricultural Chemicals Division, Richmond, CA . MRID No. 409276-01.

REVIEWED BY:

Clinton L. Fletcher
Chemist, EFGWB/EFED

Signature: 
Date: 2-21-89

APPROVED BY:

Paul J. Mastradone
Acting Chief, Section 1, EFGWB/EFED

Signature: 
Date:

TYPE OF STUDY: Aerobic Aquatic Metabolism

CONCLUSIONS:

1. This study is scientifically sound and satisfies the data requirement for an aerobic aquatic metabolism study.
2. Based on the results of this study, EFGWB concludes that diquat residues will not degrade under aerobic aquatic conditions in the environment. Under conditions maintained in the laboratory, there was no degradation of ^{14}C -diquat in the aerobic aquatic metabolism study. The data indicate that throughout the study 95% to 99% of the ^{14}C -diquat residues were associated with the soil sediment. No aerobic aquatic half-life could be calculated.

MATERIALS AND METHODS:

Radiolabelled diquat (See Figure 1a for position of radiolabels) with a specific activity of 51.9 mCi/mM and 99.9% radiochemically pure active ingredient was used in this study.

Samples of pond sediment (92% sand, 4% silt, 4% clay, 0.5% OM, pH 7.6) were flooded with microbially viable pond water (pH 7.8) representative of an intended use site in Florida and treated with 2.667 ug radiolabelled diquat ion equivalents per gram of sediment. Samples were incubated under aerobic conditions in the dark and maintained at 25^o C for a total of 31 days. A series of traps were maintained during the study to trap any volatile products formed (ethylene glycol and 1 N H₂SO₄ to trap organics and 1N KOH to trap CO₂).

Samples were taken at days 0, 1, 7, 14, 21, and 31 after treatment. After each sampling period, the separated soil/water fractions were maintained at -22C until completion of the study. Soil samples were analyzed for extractable and bound residues. Aqueous fractions were refluxed. Extractable residues from soil and water were analyzed using liquid scintillation counting (LSC) for material balance, qualitatively by thin-layer chromatography (TLC) and autoradiography and quantitated using High performance Liquid Chromatography (HPLC). Non-extractable were measured using soil combustion techniques. The ¹⁴C-residues were characterized as volatile residues, water residues and extractable and non-extractable soil residues. Total soluble residues were calculated as the sum of the water and extractable soil residues.

Reported Results:

The author reported the mass balance as being 78-108% (mean value of 96.8% with std. dev. of 13.3%). Mass Balance for day 0 was reported as 16.1% which was attributed to a dosing error. No volatile degradation products were found. No degradation products were found by HPLC analysis. Diquat was the only compound detected in any of the extracts. Since there was no degradation over the course of the study, no degradation half-life could be calculated.

The author reported that diquat accounted for 98.4% (std. dev. = 2.0%) of the total soluble ¹⁴C-residues present at any sampling period and that 95-99% of the applied radiolabelled diquat residues were associated with the sediment.

DISCUSSION:

1. This study is scientifically sound and satisfies the requirement for an aerobic aquatic metabolism study as required under Subdivision N of the Guidelines. No storage stability data were submitted. However, considering the results of the study, such data are not necessary.
2. Based on the results reported in the study, EFGWB concludes that diquat will not degrade under aerobic aquatic conditions in the environment. The data indicate that in the aquatic environment diquat would be primarily associated with the soil sediment (even a soil with 92% sand).

TABLE V

CHARACTERIZATION OF THE STUDY SOIL AND WATER
FOR AEROBIC AQUATIC METABOLISM OF ¹⁴C-DIQUAT^a

Percent Organic Matter	(1/3 bar Moisture) Percentage	Field Capacity C.E.C. ^b MEQ/100	Percent			pH	Bulk Density	Soil Texture
			Sand	Silt	Clay			
0.5	2.12	3.4	92	4	4	7.6	1.55	Sand

Water pH at time of receipt was 7.83.

^aNote: All soil analysis conducted by A & L Laboratories, Inc. of Omaha, Nebraska.

^bC.E.C. = Cation Exchange Capacity

TABLE VI

DISTRIBUTION OF TOTAL ¹⁴C-RESIDUES WITHIN TEST SAMPLES
DURING DIQUAT AEROBIC METABOLISM STUDY^a

Day	Total Residue		Soil ^b	Extractable Soil	Non-Extractable Soil	Total Soluble ^c	% Diquat by HPLC ^d		% Accountability ^e
	Water	Soil ^b					HPLC ^d	%	
0	0.43	0.04	0.39	0.39	0.00	0.43	94.2	16.1	
1	2.68	0.11	2.56	2.55	0.01	2.66	98.1	100.1	
2	2.84	0.05	2.79	2.79	0.00	2.84	100.0	106.1	
7	2.84	0.09	2.75	2.75	0.00	2.84	100.0	106.1	
14	2.09	0.03	2.06	2.06	0.00	2.09	99.3	78.1	
21	2.88	0.02	2.86	2.85	0.01	2.87	99.1	107.6	
31	2.18	0.02	2.16	2.15	0.01	2.17	98.4	81.4	

^a All values in $\mu\text{g/g}$ except "% Diquat by HPLC" and "% Accountability".

^b Extractable soil and non-extractable soil residues.

^c Water and extractable soil residues.

^d (Diquat by HPLC of water + diquat by HPLC of soil extract)/total residue.

^e (Total residue/initial dose) x 100.

DEGRADATION RATE OF ¹⁴C-DIQUAT DURING THE AEROBIC
AQUATIC METABOLISM STUDY

Days After Application	% of Dose as Diquat Ion ^a					
	Soil Extract	+	Aqueous Residues	=	Total Diquat	ln % Total Diquat
0	13.7		1.5		15.2	2.721
1	93.8		4.1		97.9	4.584
2	104.2		1.9		106.1	4.664
7	101.2		3.4		104.6	4.650
14	77.5		1.1		78.6	4.364
21	105.5		0.74		106.2	4.666
31	79.0		0.75		79.8	4.379

$$y = -0.0065x + 4.646$$

$$r^2 = 0.280$$

$$p = 0.28$$

^a As analyzed by HPLC, applied dose = 2.677 μg diquat ion equivalents/g of soil.

(Table VIII, continued...)

TABLE VIII (continued)

DEGRADATION RATE OF ^{14}C -DIQUAT DURING THE AEROBIC
AQUATIC METABOLISM STUDY

Model: MODEL1
Dependent Variable: LC

Analysis of Variance

<u>Source</u>	<u>DF</u>	<u>Sum of Squares</u>	<u>Mean Square</u>	<u>F Value</u>	<u>Prob>E</u>
Model	1	0.02922	0.02922	1.551	0.2809
Error	4	0.07533	0.01883		
C Total	5	0.10455			

Root MSE	0.13724
Dep Mean	4.56437
C.V.	3.00667
R-square	0.2795
Adj R-sq	0.0993

Parameter Estimates

<u>Variable</u>	<u>DF</u>	<u>Parameter Estimate</u>	<u>Standard Error</u>	<u>T for HO: Parameter=0</u>	<u>Prob> T </u>
INTERCEP	1	4.646839	0.08673248	53.577	0.0001
DAY	1	-0.006511	0.00522700	-1.246	0.2809

TABLE IX

¹⁴C-VOLATILES IN TRAPPING SOLUTION IN μg ¹⁴C-DIQUAT ION EQUIVALENTS

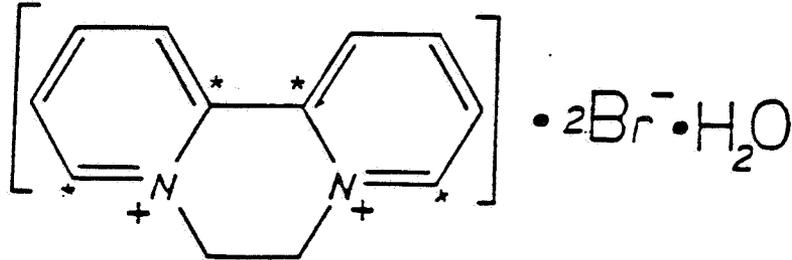
	Days After Application					
	1	2	7	14	21	30
<u>Total μg Diquat Equivalents</u>						
Et	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024
H	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024
K ₁ + K ₂	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024
Total g Soil in System	80	70	60	50	40	30
<u>μg Diquat Equivalents/g of Soil</u>						
Et	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024
H	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024
K ₁ + K ₂	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024
<u>Accumulative</u>						
<u>μg Diquat Equivalents/g of Soil</u>						
Et	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024
H	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024
K ₁ + K ₂	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024

Note: Et = Ethylene Glycol trapping solution
H = H₂SO₄ trapping solution
K₁ = First KOH trapping solution
K₂ = Second KOH trapping solution

Note: Limit of detection = 2 x background = 0.024 μg diquat ion equivalents (0.001 $\mu\text{g}/\text{g}$ soil)

FIGURE 1a

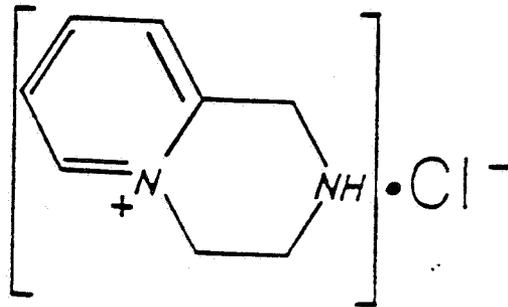
STRUCTURE AND NOMENCLATURE OF ^{14}C -DIQUAT
AND SUSPECTED DEGRADATION PRODUCTS



^{14}C -Diquat
[4,9,13,14- ^{14}C]9,10-dihydro-8a,10a-diazoniaphenanthrene
ion (as dibromide monohydrate)

*Denotes position of label

FIGURE 1b



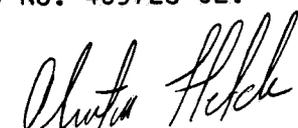
TOPPS
1,2,3-tetrahydro-1-oxopyrido[1,2-a]
Pyrazin-5-ium ion (as chloride)

DATA EVALUATION RECORD

STUDY IDENTIFICATION: Johnson, J. J., 1988. Anaerobic Aquatic Metabolism of Diquat. Laboratory Project Identification MEF-0072. Chevron Chemical Co., Ortho Agricultural Chemicals Division, Richmond, CA. MRID No. 409723-02.

REVIEWED BY:

Clinton L. Fletcher
Chemist, EFGWB/EFED

Signature: 

Date: 2-21-89

APPROVED BY:

Paul J. Mastradone
Acting Chief, Section 1, EFGWB/EFED

Signature: 

Date: FEB 21 1989

TYPE OF STUDY: Anaerobic Aquatic Metabolism

CONCLUSIONS:

1. This study is scientifically sound and satisfies the data requirement for an anaerobic aquatic metabolism study as required under Subdivision N of the Guidelines.
2. Based on the results of this study, EFGWB concludes that diquat will not degrade under anaerobic aquatic conditions in the environment. Under conditions maintained in the laboratory, there was essentially no degradation of ¹⁴C-diquat in the anaerobic aquatic metabolism study after nine months incubation. One minor compound was noted after 3 months but was not identified. After nine months, this compound accounted for about 5% of the applied diquat residues. The data indicate that throughout the study 89 -100% of the ¹⁴C-residues were associated with the soil sediment. No degradation half-life could be calculated.

MATERIALS AND METHODS:

Radiolabelled diquat (See Figure 1a for position of the radiolabels) with a specific activity of 51.9 mCi/mM and 99.9% radiochemically pure active ingredient was used in this study.

Samples of pond sediment (92% sand, 4% silt, 5% clay, 0.5% Om, pH 7.6) were flooded with pond water (pH 7.8) and aged under nitrogen atmosphere for 35 days prior to treatment. Samples were then treated with 2.677 ug diquat ion per gram sediment and incubated under anaerobic conditions in the dark at 25° C for up to nine months. A series of traps were maintained during the study to trap any volatile organic compounds and/or CO₂ which may be produced.

Samples were taken at days 0, 1, 7, 14, 21, 31, 62, 91, 122, 183, and 274 days after treatment. After each sampling period the aqueous fraction was decanted and both fractions were stored at -22C until analysis. Soil samples were analyzed for extractable and non-extractable residues. Aqueous samples were refluxed. Extractable residues from soil and water were analyzed using liquid scintillation counting (LC) for material balance, qualitatively by thin-layer chromatography (TLC) and autoradiography, and quantitated using High Performance Liquid Chromatography (HPLC). Non-extractable residues were quantitated using soil combustion techniques. The ¹⁴C-residues were characterized as volatile residues, water residues and extractable and non-extractable soil residues. Total soluble residues were calculated as the sum of water and extractable soil residues.

REPORTED RESULTS:

The author reported the mean mass balance throughout the study as being 98.9% ± 8.1% (range 87.2 - 111.6%) of the applied dose. No volatile degradation products were found. Diquat was the primary ¹⁴C residue present in any sample at all sampling times. A minor degradation product was found at the 3 month interval. However, after 9 months incubation, this minor compound accounted for only 5.5% of the applied residues.

The author reported that diquat accounted for 94.7% (std. dev. = 4.3%) of the soluble ¹⁴C residues present at all sampling periods. It was calculated that 89 -100% of the ¹⁴C-residues were associated with the sediment throughout the study.

DISCUSSION:

1. This study is scientifically sound and satisfies the requirement for an anaerobic aquatic metabolism study as required by Subpart N of the Guidelines. No storage stability data were submitted. However, considering the results of the study, none are necessary.
2. Based on the results of the study, EFGWB concludes that diquat will not degrade under anaerobic aquatic conditions in the environment. The data indicate that in the aquatic environment, diquat residues will be associated with the soil sediment (even a soil consisting of 92% sand).

TABLE VI

DISTRIBUTION OF TOTAL ¹⁴C-RESIDUE WITHIN SAMPLES DURING DIQUAT ANAEROBIC AQUATIC METABOLISM STUDY

Sample	Total Residue	Water	Soil ^b	Extractable Soil	Non-Extractable Soil	Total Soluble ^c	% Diquat by HPLC ^d	% Minor Compound by HPLC ^e	% Accountability ^f
0 day	2.67	0.05	2.62	2.62	0.01	2.67	98.8	0.0	100.0
1 day	2.69	0.05	2.64	2.64	0.01	2.69	97.0	0.0	100.3
3 day	2.40	0.08	2.32	2.32	0.00	2.40	100.0	0.0	89.9
7 day	2.63	0.08	2.62	2.62	0.00	2.70	100.0	0.0	98.5
14 day	2.47	0.07	2.40	2.40	0.00	2.47	98.1	2.7	92.5
1 month	2.47	0.09	2.38	2.36	0.01	2.45	91.4	8.2	92.5
2 month	2.98	0.36	2.64	2.63	0.01	2.97	92.0	7.9	111.6
3 month	2.31	0.08	2.23	2.22	0.01	2.30	89.6	9.5	86.5
4 month	2.40	0.03	2.37	2.37	0.02	2.38	89.6	8.8	89.9
6 month	2.33	0.05	2.28	2.27	0.01	2.32	90.4	7.5	87.2
9 month	2.45	0.04	2.41	2.40	0.01	2.44	94.1	5.5	91.7

^a All values in $\mu\text{g/g}$ except % Diquat by HPLC, % Minor Compound by HPLC and % Accountability.

^b Extractable soil and non-extractable soil residues.

^c Water and extractable soil residues.

^d (Diquat by HPLC of water extract + diquat by HPLC of soil extract)/total residue.

^e (Minor compound by HPLC of water extract + minor compound by HPLC of soil extract)/total residue.

^f (Total residue/initial dose) x 100.

TABLE IX

¹⁴C-VOLATILES IN TRAPPING SOLUTION IN μg ¹⁴C-DIQUAT ION EQUIVALENTS

	Days After Application											
	1	3	7	14	31	62	91	122	183	274		
<u>Total μg Diquat Equivalents</u>												
Et	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024
H	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024
K ₁ + K ₂	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024
Total g Soil in System	176	160	150	140	130	120	110	90	80	70		
<u>μg Diquat Equivalents/g of Soil</u>												
Et	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024
H	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024
K ₁ + K ₂	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024
<u>Accumulative</u>												
<u>μg Diquat Equivalents/g of Soil</u>												
Et	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024
H	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024
K ₁ + K ₂	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024

Note: Et = Ethylene Glycol trapping solution
H = H₂SO₄ trapping solution
K₁ = First KOH trapping solution
K₂ = Second KOH trapping solution

Note: Limit of detection = 2 x background = 0.024 μg diquat ion equivalents (0.001 $\mu\text{g/g}$ soil)

DEGRADATION RATE OF ^{14}C -DIQUAT DURING THE ANAEROBIC
AQUATIC METABOLISM STUDY

% of Dose as Diquat Ion ^a						
<u>Days After Application</u>	<u>Soil Extract</u>	<u>+</u>	<u>Aqueous Residues</u>	<u>=</u>	<u>Total Diquat</u>	<u>In % Total Diquat</u>
0	96.4		1.8		98.2	4.587
1	98.1		1.8		99.9	4.604
3	86.9		2.9		89.9	4.499
7	98.1		2.9		101.0	4.615
14	88.2		2.5		90.7	4.508
1 month (31)	81.0		3.1		84.1	4.432
2 month (62)	90.8		12.3		103.1	4.636
3 month (92)	74.8		2.7		77.5	4.350
4 month (122)	79.3		1.0		80.3	4.385
6 month (183)	76.9		1.7		78.6	4.364
9 month (274)	84.8		1.4		86.2	4.457

$$y = -.000656x + 4.5416$$

$$r^2 = 0.312$$

$$p = 0.074$$

^a As analyzed by HPLC, applied dose = 2.677 μg diquat ion equivalents/g of soil.

(Table VIII, continued...)

DEGRADATION RATE OF ¹⁴C-DIQUAT DURING THE AEROBIC
AQUATIC METABOLISM STUDY

Model: MODEL1
Dependent Variable: LC

Analysis of Variance

<u>Source</u>	<u>DF</u>	<u>Sum of Squares</u>	<u>Mean Square</u>	<u>F Value</u>	<u>Prob>E</u>
Model	1	0.03460	0.02922	4.099	0.0736
Error	9	0.07596	0.00844		
C Total	10	0.11056			

Root MSE	0.09187
Dep Mean	4.49449
C.V.	2.04409
R-square	0.3129
Adj R-sq	0.2366

Parameter Estimates

<u>Variable</u>	<u>DF</u>	<u>Parameter Estimate</u>	<u>Standard Error</u>	<u>T for HO: Parameter=0</u>	<u>Prob> T </u>
INTERCEP	1	4.541546	0.03615992	125.596	0.0001
DAY	1	-0.000656	0.00032405	-2.025	0.0736

DATA EVALUATION RECORD

STUDY IDENTIFICATION: Tegala, B. and M. W. Skidmore. 1987. Diquat: An Aqueous Photolysis Study. Laboratory Project Identification No. RJ 0613B. Chevron Chemical Co., Ortho Agricultural Chemicals Division, Richmond CA. MRID No. 404188-01.

REVIEWED BY:

Clinton L. Fletcher
Chemist, EFGWB/EFED

Signature: 

Date: 2-21-89

APPROVED BY:

Paul J. Mastradone
Acting Chief, Section 1, EFGWB/EFED

Signature: 

Date: FEB 21 1989

TYPE OF STUDY: Aqueous Photolysis

CONCLUSIONS:

1. This study, while not conducted to the SEP standards, is overall scientifically sound and will satisfy the requirement for an aqueous photolysis study as required under Subdivision N of the Guidelines.
2. Based on the results of the study, EFGWB concludes that diquat would be considered photolytically stable in the aquatic environment. The calculated half-life is 74 days under Florida spring sunlight. The 1,2,3,4-tetrahydro-1-oxopyrido (1,2-a) pyrazin-5-ium ion (See Figure 1b for structure) was the major photolytic degradation product. Four other products in small amounts (<5% each) were observed but not identified.

MATERIALS AND METHODS:

Radiolabelled diquat (See Figure 1a for position of radiolables) with a specific activity of 4.189mCi/mM and >99.1% radiochemical purity and unlabeled analytical standard diquat with 100% purity were used in this study.

Sterile buffered (to pH 7) were treated with ¹⁴C-diquat at concentration of approximately 20ug ml⁻¹ in sterile photolysis vessels with quartz lids. The photolytic light source was a Suntest xenon arc lamp filtered to approximate natural sunlight. The test vessels were maintained at 25^o C under positive air pressure and irradiated continuously for up to 300 hours which was equivalent to 32 days of Florida spring sunlight. A series of traps were maintained to

trap any volatile compounds which may form during the test exposure period. Samples were taken at times which approximated 0, 8, 15, 24, and 32 days of Florida spring sunlight. At each sampling period, a test vessel was removed and stored at -15C prior to analysis of sample solutions. Dark controls were also maintained. Day zero samples were taken and stored at -15C until analysis. The material balance of the ¹⁴C residues in the samples was determined by liquid scintillation counting (LSC). Extracted residues were analyzed thin-layer chromatography (TLC) using co-chromatography of known standards. Quantitation was by using linear scanning/autoradiography of the TLC plate.

REPORTED RESULTS:

The authors report that, based on the calculations relating the length of irradiation to that of a Florida spring day, diquat had a photolytic half-life of 74 days. After irradiation approximating 32 days of Florida sunlight 73% of the applied ¹⁴C was recovered as diquat. The 1,2,3,4-tetrahydro-1-oxopyrido (1,2-a) pyrazin-5-ium ion which accounted for 12% of the applied radioactivity and four other degradates (unidentified) were found. None of the other four degradates accounted for more than 5% of the applied radiolabel. No volatile degradation products were found.

No degradation was noted in the dark controls or in the zero day samples.

DISCUSSION:

1. This study, while not conducted to the SEP standards, is overall scientifically sound and will satisfy the requirement for an aqueous photolysis study as required under Subdivision N of the Guidelines.

The study is deficient in that: (1) it was not conducted for 30 (calendar) days with periods of light (irradiation) and darkness. (However, calculations were presented which show that the irradiation time approximated 32 days of Florida spring sunlight.); (2) linear scanning of TLC plates is not quantitative analysis, but considering the results of the study, it will suffice for this study; (3) No storage stability data were submitted. However results of the zero day samples will suffice for this data.

2. Based on the results of the study, EFGWB concludes that diquat will photodegrade slowly with a half-life of about 74 days in the aquatic environment without sediment. The 1,2,3,4-tetrahydro-1-oxopyrido (1,2-a) pyrazin-5-ium ion appears to be the major photodegrade.
3. However, in the aquatic environment with sediment, EFGWB does not consider photolysis as a means of diquat dissipation.

4. This reviewer notes the results of this study are not consistent with previously reviewed data which indicate that diquat quickly photodegrades in aqueous solution exposed to sunlight (Enviro Control, Inc., "Task 1R: Review of Diquat", prepared for U. S. EPA under contract no. 68-01-5830, January 16, 1981.). However, there were no dark controls in this study. Thus, it could not be determined whether the degradation was due to photolysis or other degradation mechanisms. This study was not accepted as satisfying the Subdivision N Guideline data requirement.

Table 5 shows results from TLC analysis of the aqueous photolysis solutions. The values given, represent the mean from TLC using at least two solvent systems. An example calculation, showing how the values are derived, is given in Appendix 7. TLC analysis results from each solvent system are shown in Appendix 8.

TABLE 5 : Mean Values from TLC Analysis of Aqueous Photolysis Solutions (expressed as a % of the total radioactivity recovered)

Sample	% Diquat	% Compound 2	% Baseline	% Unknown Compounds	% Remainder ^e
Dark Control A	97.9	ND	ND	ND	2.1
Dark Control B	97.6	ND	ND	ND	2.4
Zero A (0 day)	97.7	ND	ND	ND	2.3
Zero B (0 day)	98.0	ND	ND	ND	2.0
1A (8 day)	89.7	3.4	1.2	2.9 ^a	2.6
1B (8 day)	92.1	2.4	1.2	1.4 ^a	2.7
2A (15 day)	88.4	4.4	1.1	3.0 ^a	3.0
2B (15 day)	84.1	6.0	1.6	4.2 ^a	4.0
3A (24 day)	80.3	6.6	6.2	4.6 ^b	2.0
3B (24 day)	79.9	9.1	2.0	5.5 ^b	3.2
4A (32 day)	73.9	11.8	1.1	7.0 ^c	5.7
4B (32 day)	72.7	11.9	1.6	7.4 ^d	5.9

ND = not detected

a = at least two compounds

b = at least four compounds

c = at least three compounds, none representing more than 5.3% of the radioactivity

d = at least three compounds, none representing more than 4.6% of the radioactivity

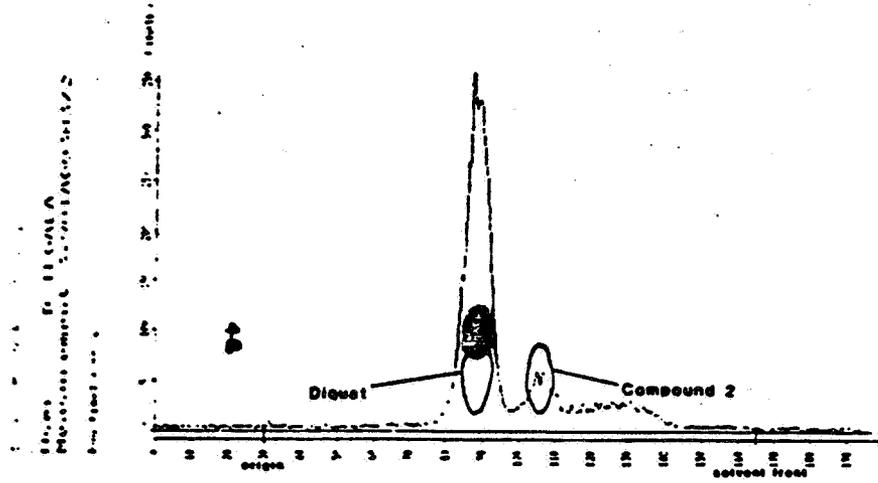
e = "Remainder" refer. to the summation of areas, on the radiochromatogram, which integrate above background but contain no discrete areas of radioactivity. This probably represents a mixture of machine noise, and radioactivity "streaking" along the chromatoplate. Diquat and its highly polar breakdown products are known to cause "streaking" of radioactivity on chromatoplates.

Figure 6

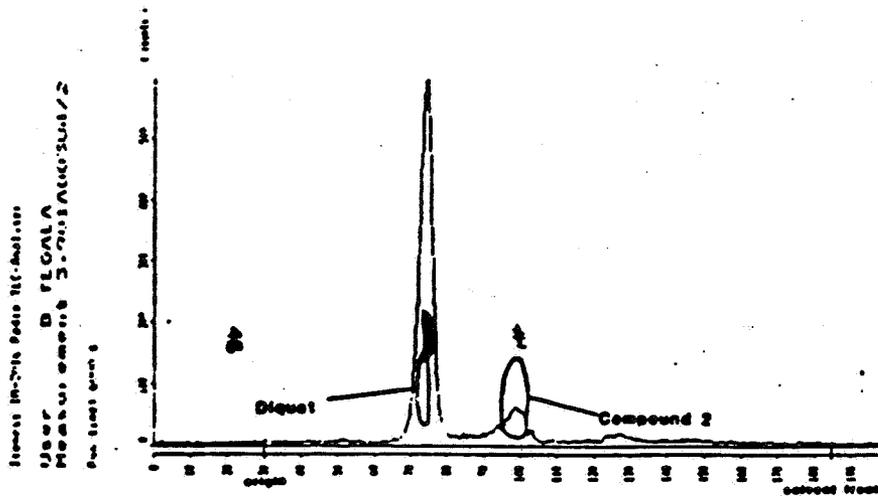
Radiochromatograms and Autoradiograms from Thin Layer

Chromatograms of Sample 4B (32 day)

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Page 23



Solvent System 2



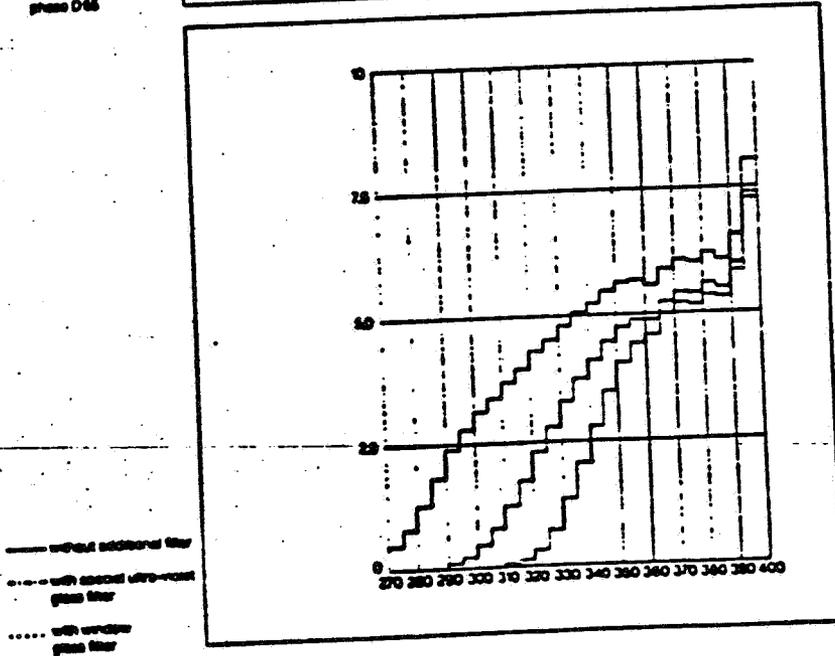
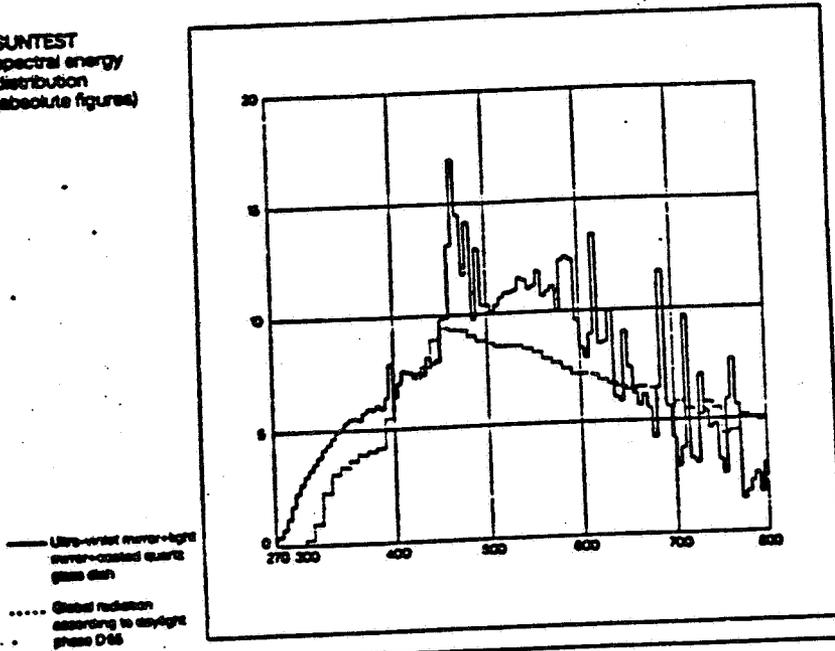
Solvent System 10

U = Standard Reference Marker

FIGURE 9 : Comparison of Spectral Distribution of Suntest Radiation with D65 Radiation

The additional special ultra-violet glass filter is used.

SUNTEST
spectral energy
distribution
(absolute figures)



DATA EVALUATION RECORD

STUDY IDENTIFICATION: Pack, D. E.. 1987. Diquat Volatility - -Laboratory Study. Laboratory Project Identification No. MEF-0045. Chevron Chemical Co. Ortho Agricultural Chemicals Division, Richmond, CA. MRID No. 402451-01.

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Chemist, EFGWB/EFED

Signature: *Clinton Fletcher*

Date: 2-21-87

APPROVED BY:

Paul J. Mastradone
Acting Chief, Section 1, EFGWB/EFED

Signature: *Paul J. Mastradone*

Date: FEB 21

TYPE OF STUDY: Laboratory volatility.

CONCLUSIONS:

1. This study is a one page interim statement concerning diquat's volatility. Diquat has a vapor pressure of $<4 \times 10^{-9}$ mm Hg at 25°C. According to DEB/HED (R. Perfetti), this data requirement is satisfied.

This submission contains other reports (e.g., photolytic stability on soil surfaces, plant surfaces, evaporation from surfaces of aluminum planchets).

PAGE 27 IS NOT INCLUDED WITH THIS REVIEW. INFORMATION REVEALING SUPPLIER, PRODUCT CHEMISTRY DATA, AND QUALITY CONTROL PROCEDURES WAS CONTAINED ON THAT PAGE.