

US EPA ARCHIVE DOCUMENT

PROPRIETARY

Date Out EFB: JUL 27 1981

To: Product Manager ~~21 Jacoby~~ 23 (Mountfort)
TS-767

From: Dr. Willa Garner *SAC for*
Chief, Review Section No. 1
Environmental Fate Branch

Attached please find the environmental fate review of:

Reg./File No.: 464-LAG, 1F2439, 1H5280

Chemical: 2,4-D and 3,6-dichloropicolinic acid

Type Product: Herbicide

Product Name: LONTREL 205 Herbicide

Company Name: Dow

Submission Purpose: registration on spring and winter wheat, barley and oats
not underseeded with a legume

ZBB Code: 3(c)(5)

ACTION CODE: 110, 225, and 215

Date in: 11/21/80

EFB # 681, 682, and 683

Date Completed: JUL 27 1981

TAIS (level II)

Days

Deferrals To:

61

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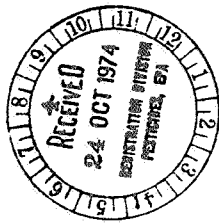
 Ecological Effects Branch

 Residue Chemistry Branch

 Toxicology Branch

1. INTRODUCTION

- 1.1 This is a registration request for the new chemical 3,6-dichloropicolinic acid to control broadleaf weeds in spring and winter wheat, barley and oats not underseeded with a legume. The new chemical is to be used in the product LONTREL 205 Herbicide and will contain, as active ingredients, 3,6-dichloropicolinic acid as alkanolamine salts (of the ethanol and isopropanol series) at 0.5 lb/gal and 2,4-D as alkanolamine salts (of the ethanol and isopropanol series) at 2.0 lb/gal.
- 1.2 See the review of the EUP (464-EUP-55) dated April 9, 1979.
- 1.3 Structure
- 1.4 The ai, 3,6-dichloropicolinic acid is also known as 3,6-dichloro-2 pyridinecarboxylic acid.
- 1.5 The PM states in the Submission Review Record (attached) that 2,4-D is already registered for the proposed uses (464-507).



AMINE-FOUR HERBICIDE

Contains Alkanolamine Salts† of 2,4-D Acid Equivalent: 4 Pounds per Gallon
For Selective Control of Many Broadleaf Weeds in Non-Crop Areas, Grass Pastures,
Rangelands, and in Certain Crops Also for Control of Trees by Injection

ACTIVE INGREDIENTS: Alkanolamine Salts* (of the Ethanol series) of 2,4-Dichlorophenoxyacetic acid . . . 57.1%
INERT INGREDIENTS: . . . 42.9%

2,4-Dichlorophenoxyacetic Acid Equivalent 38.7% 4 lb/gal

E.P.A. Reg. No. 464-507-AA

E.P.A. Est. 464-MI-1

*Salts are the least volatile forms of 2,4-D and do not release enough vapors from treated areas to reduce yields of adjacent susceptible crops.

CAUTION

KEEP OUT OF REACH OF CHILDREN
HARMFUL IF SWALLOWED

CAUSES IRRITATION OF SKIN AND EYES
Do Not Get in Eyes, on Skin or on Clothing

In case of contact, flush eyes with plenty of water for at least 15 minutes and get medical attention; wash skin with soap and plenty of water. Remove and wash contaminated clothing before reuse. Do not wear contaminated shoes.

AGRICULTURAL CHEMICAL

Do Not Ship or Store with Food, Feeds, or Clothing

PRECAUCION AL USUARIO: Si usted no lee inglés, no use este producto hasta que la etiqueta le haya sido explicada ampliamente.

TRANSLATION: (TO THE USER: If you cannot read English, do not use this product until the label has been fully explained to you.)

5 GAL/18.9 L

2. DIRECTIONS FOR USE

- 2.1 Apply 1-2 pints of LONTREL 205 per acre to actively growing weeds. This is equivalent to 0.0625-0.125 lb ai/A.
- 2.2 Spray after grain begins tillering and before the boot stage (usually 4-8 inches tall). Avoid spray drift.
- 2.3 Do not permit dairy animals or meat animals being finished for slaughter to forage or graze treated grain fields within 1 week after treatment.
- 2.4 It is assumed from the label directions that only one application per season is being made.

3. DISCUSSION OF DATA

- 3.1 The Photolysis and Hydrolysis Rates of 3,6-Dichloropicolinic Acid in Buffered, Distilled Water and in Canal Water, R.W. Meikle, Dow Chemical, July 15, 1974, acc. no. 099728, tab D.2.

Procedure

Solutions of 3,6-dichloropicolinic acid-2, 6-¹⁴C₂ buffered to 4.7, 6.9 and 8.1 and a solution in canal water were exposed to simulated sunlight. The KIMAX glass vessels did not transmit light below 280 nm and the solutions were kept at 25 °C. There were no control samples. Analysis was by TLC followed by scraping and scintillation counting.

Results

Initial ppm	pH	Time days	% of initial remaining
2.9	6.9	1	100
		8	99.3
		21	99.0
		30	100
		60	97.5
2.2	4.7	30	100
1.5	8.1	30	100
3.5	8.0	31	100

(canal water)

Conclusions

- 1) The compound, 3,6-dichloropicolinic acid, will not photodegrade in water. It is also stable to hydrolysis under conditions expected in the environment.
- 2) Loss by volatilization did not occur.

3.2 The Photolysis and Hydrolysis Rates of 3,6-Dichloropicolinic Acid in Canal Water, II: Exposure to Sunlight, R.W. Meikle, Dow Chemical, February 4, 1975, GS-1391, acc. no. 099728, tab D.3.

Procedure

Canal water, pH=8.0, from the Contra Costa Canal, which is part of the California Central Valley Irrigation Project, was filtered and centrifuged. The water contained 0.15 ppm iron and <0.05 ppm copper. The temperature during exposure ranged from 24-38 °C.

Exposure was carried out using sunlight. No control (dark) was run. Daily exposure lasted 4-6 hours for a total of 121 hours. Exposure was spaced evenly about solar noon.

Analysis was by TLC followed by scraping and counting.

Results

Photolysis of 3,6-Dichloropicolinic Acid in Canal Water

<u>Time (hrs)</u>	<u>% of Initial Remaining (0.61 ppm initial)</u>
5	95.5
11	
21.5	96.5
82	97.5
121	100

Conclusions

- 1) The compound, 3,6-dichloropicolinic acid, will not photodegrade in natural water under sunlight under the test conditions. It also will not hydrolyze in natural water under the test conditions.
- 2) Loss by volatilization did not occur.

- 3.3 A Laboratory Study of the Photodecomposition of Carbon-14 Labeled 3,6-Dichloropicolinic Acid on Soil Surfaces, R.L. Swann and S.M. Unger, Dow Chemical, June 23, 1980, GH-C 1334, acc. no. 099728, tab D.4.

Procedure

A Cecil sandy loam (70% sand, 16% silt, 14% clay, 0.85 % OC, pH=6.4) was fortified to 1 ppm with 3,6-DPA labeled in the ring at positions 2 and 6. Twenty-five grams of the fortified soil was evenly spread on a 5" round pyrex plate to about 2 mm thick and allowed to dry in the dark. Three samples were exposed to a sunlamp for 28 days and 3 controls were kept.

CO₂-free air was drawn through the photolysis apparatus at 10-20 cc per minute, then through a PUF plug and a CO₂ trap. Soil was analyzed by combustion and by an extraction/combustion and an extraction/TLC/LSC procedure.

Results

All activity was found to be associated with the soil. Analysis showed only parent compound to be present.

Conclusions

- 1) 2,6-DPA will be stable to soil surface photolysis.
- 2) No volatilization from soil surfaces will occur.

- 3.4 DOWCO 290 (3,6-Dichloropicolinic Acid) Aerobic Soil Degradation Study, R.L. Swann et. al., Dow Chemical, GH-C 910, acc. no. 099728, tab D.5

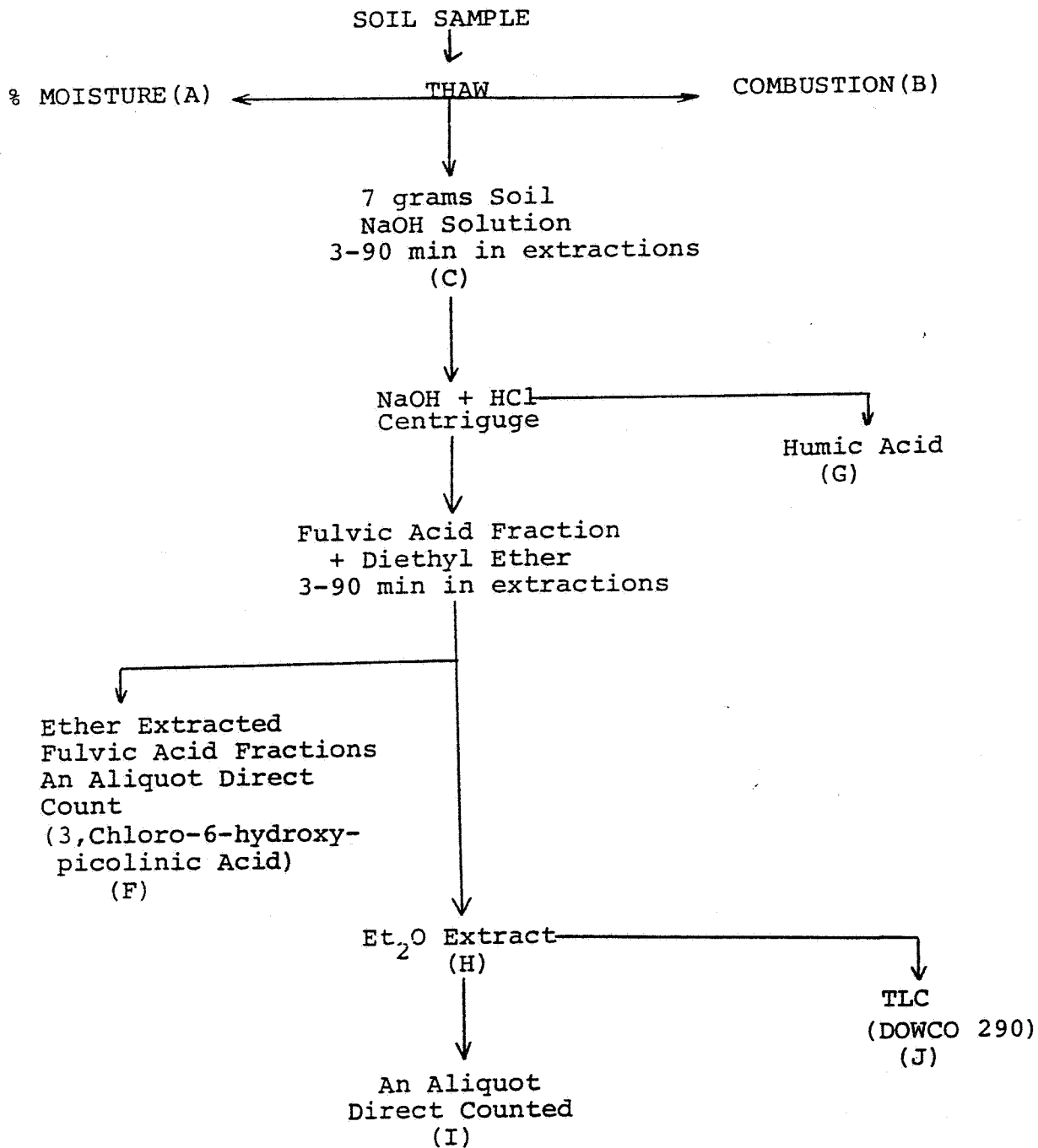
Procedure

Ten different soils described below) were sieved through a 2 mm screen, fortified to 0.25 ppm with 3,6-dichloropicolinic acid (¹⁴C-labelled in the 2 and 6 positions) and to 100% of 1/3 bar moisture and were incubated at 25 °C. It is not known if the study was run in dark; however, photolysis data show the parent compound to be stable to light.

Respired CO₂ was collected and the soil was analyzed using standard extraction and radioanalytical techniques.

PROPERTIES AND GEOGRAPHICAL SOURCE OF SOILS USED IN DOWCO 290
DEGRADATION STUDY

Soil	Source	1/3 Bar % Moisture	% Sand	% Silt	% Clay	pH	% Organic Matter
S ₁	Mississippi	17.8	42	49	9	6.2	0.5
S ₂	Illinois	26.3	14	54	32	5.8	4.2
S ₃	Oregon	26.8	15	52	33	5.2	1.85
S ₄	N. Dakota	28.1	50	30	20	7.5	27.4
S ₅	Montana	25.5	19	50	31	7.7	1.25
S ₆	S. Dakota	31.3	30	53	17	6.5	3.36
S ₇	California	19.0	50	34	16	6.5	0.8
S ₈	Oregon	28.7	21	60	19	6.1	1.32
S ₉	Montana	19.8	29	40	31	6.1	1.46
S ₁₀	Michigan	13.1	65	17	18	7.1	1.30



FLOW CHART FOR SOIL ANALYSIS

Results

- 1) For the 10 soils, 90.1 - 97.4% of the initial activity was recovered.

2,4-D/Clorpryalid EFB review

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3)

Soil Halflives of DOWCO 290

	<u>Soil Source</u>	<u>Halflife (days)</u>
S 1	Wayside, Mass.	24*
S 7	Davis, Calif.	287
S 5	Bozeman, Mont.	236
S 10	Kawkawlin, Mich.	20
S 8	Pendleton, Ore.	34
S 9	Sidney, Mont.	15
S 3	Corvallis, Ore.	20
S 4	N. Dakota	15
S 6	S. Dakota	16
S 2	Geneso, Ill.	47

*This figure appears to be in error and should be 34 days.

Conclusion

- 1) Of the 10 soils studied, 8 showed a halflife for 3,6-dichloropicolinic acid of 15-47 days. The remaining 2 showed a halflives of 236 and 287 days. No reason could be found to explain this divergence except microbial adaptation.
- 2) The parent compound degraded releasing large amounts of $^{14}\text{CO}_2$ indicating ring cleavage.
- 3) Only parent compound was found in the soil extracts with the exception of the ether extracted fulvic acid fraction which contained 3-chloro-6-hydroxypicolinic acid (at less than 10% of the initially applied ^{14}C).

3.5 Aerobic Soil Degradation of Carbon-14 Labeled 3,6-Dichloropicolinic Acid,
R.L. Swann et. al., Dow Chemical, June 23, 1980, GH-C 1333, acc.
no. 099728, tab. D.6

Procedure

Six soils, described below, were sieved at 2 mm, were fortified with ^{14}C -3,

<u>Series</u>	<u>Class</u>	<u>pH</u>	<u>% OC</u>	<u>% Sand</u>	<u>% Silt</u>	<u>% Clay</u>
Cecil	Sandy loam	6.3	0.65	72	14	14
Tracy	Sandy loam	6.2	1.12	56	30	14
Geneso	Sty. cl. 1m.	6.2	1.90	12	56	32
Fargo	Clay	7.4	3.77	4	34	62
Yolo	Sdy. cl. 1m.	6.9	0.59	46	28	26
Bozeman	Sty. cl. 1m.	6.2	1.46	16	52	32

6-dichloropicolinic acid (labeled in the 2 and 6 positions) to a concentration of 0.25 ppm. The fortified soils were incubated at 25 °C and 75% of the 1/3 bar moisture.

Respired CO_2 was collected and the soil was extracted and analyzed using standard radio-analytical techniques.

2,4-D/Clorpryalid EFB review

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Conclusions

- 1) Of the 6 soils studied, 4 showed halflives of 18-60 days. The other 2 showed halflives of 71 and 152 days. The large range in halflives could only be explained by microbial adaptation.
- 2) Decrease in the amount of parent compound was followed by a corresponding increase in CO₂. No other products were found.

3.6 Effect of Temperature, Moisture and Concentration on the Degradation Rate of DOWCO 290 in Soil Incubated Under Aerobic Conditions, R. L. Swann et. al., DOW Chemical, May 3, 1977, GH-C 996, acc. no. 099728, tab D.7.

Procedure

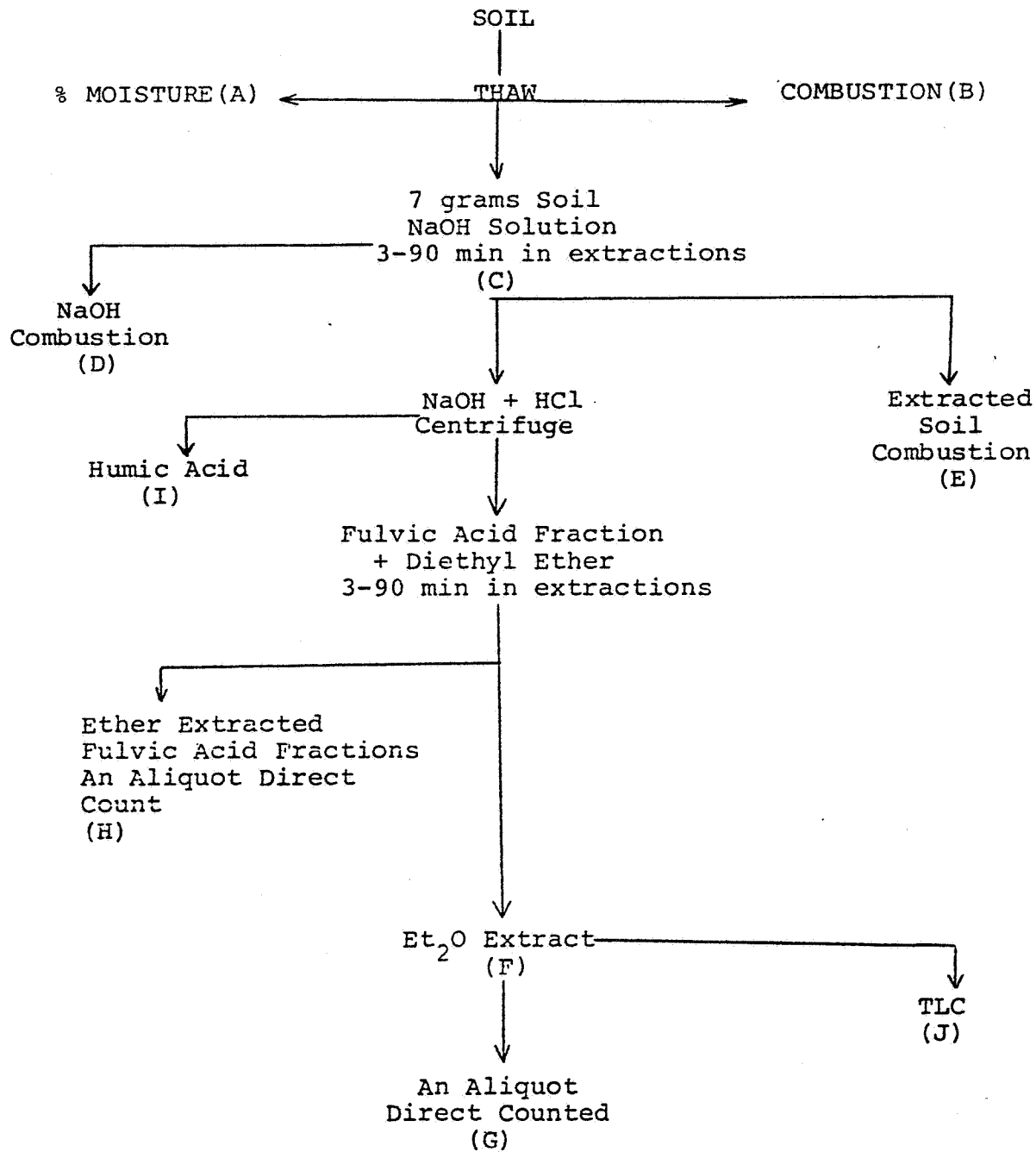
Two soils, described below, were fortified to 2 concentrations (0.25 and 1.0 ppm) and incubated at 3 temperatures (15, 25 and 35 °C) and at 5 moisture levels (air dry, 32, 50, 75 and 100% of 1/3 bar moisture).

Respired CO₂ was collected and the soil was analyzed using standard extraction and radio-analytical techniques.

The 3,6-dichloropicolinic acid was labeled in the 2 and 6 positions.

PROPERTIES AND GEOGRAPHIC SOURCE OF SOILS USED IN DOWCO 290 DEGRADATION STUDY

Soil Code	Soil Type/ Source	1/3 Bar % Moisture	% Sand	% Silt	% Clay	pH	% Organic Matter
S ₁	Commerce Wayside, MS	17.8	42	49	9	6.2	0.5
S ₂	Flanagan Geneseo, IL	26.3	14	54	32	5.8	4.2



FLOW CHART FOR SOIL ANALYSIS

2,4-D/Clorpryalid EFB review

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Conclusions

- 1) The rate of degradation of DOWCO 290 increases with temperature.
- 2) The rate of degradation of DOWCO 290 increases with soil moisture. Degradation is quickest at 75% and 100 % 1/3 bar moisture.
- 3) An initial soil fortification of DOWCO 290 of 0.25 ppm reaches a halflife quicker than does an initial fortification of 1.0 ppm. The slower degradation rate at the higher fortification could be due to a longer microbe adaptation and response time.
- 4) The degradation pathway was not changed in any of the experiments as the overall distribution of ¹⁴C activity in the different soil fractions was not altered.
- 5) The data at 25 °C, 0.25 ppm initial and 75-100% moisture are in agreement with the aerobic soil metabolism data reviewed above.

3.7 A Laboratory Study to Determine the Effect of Concentration and Carrier Solvent on the Degradation Carbon-14 Labeled 3,6-Dichloropicolinic Acid in Soil, R.L. Swann et. al., Dow Chemical, August 7, 1980, GH-C 1351, acc. no. 099728, tab D.8.

Procedure

Five soils, described below, were fortified with ¹⁴C-3,6-dichloropicolinic acid (labeled in the 2 and 6 positions) over a concentration range of 0.0025 ppm to 2.5 ppm. Three different solvent systems were used to dissolve the active ingredient; they are (1) acetone, (2) water and (3) formulation EF-258. After soil fortification, the moisture content was brought to 75% of 1/3 bar moisture, the system was connected to a CO₂ trap and was then incubated at 25 °C.

Degradation of parent compound was correlated to CO₂ production and was not determined via soil analysis. ¹⁴CO₂ production was determined by typical LSC techniques.

2,4-D/Clorpryalid EFB review

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Conclusions

The rate of release of CO₂ from 3,6-dichloropicolinic acid in soil decreases with increasing initial concentrations. Also, when acetone is used as a carrier as opposed to water, degradation through the first 1-2 half-lives is inhibited.

- 3.8 The Soil Persistence and Crop Selectivity of 3,6-Dichloropicolinic Acid, Prepared for Dow Chemical by D.L. Olson of Oregon State University Feb. 1975, acc. no. 099725, tab D.4

Conclusions

The soil was analyzed for residues of 3,6-dichloropicolinic acid using bioassay techniques. This method is not adequate in this case since metabolites are not identified and the extent of leaching is not defined. Also, in general, residues may be present which will not cause a response to the test species.

Based on the above, this study will not satisfy the requirement for a field dissipation study.

- 3.9 Comparison of ¹⁴C-DOWCO 290 Degradation in Aerobic, Aerobic/Waterlogged, and Waterlogged Soils, R.L. Swann, et. al., Dow Chemical, Feb. 15, 1977, GH-C 965, acc. no. 099727, tab D.9.

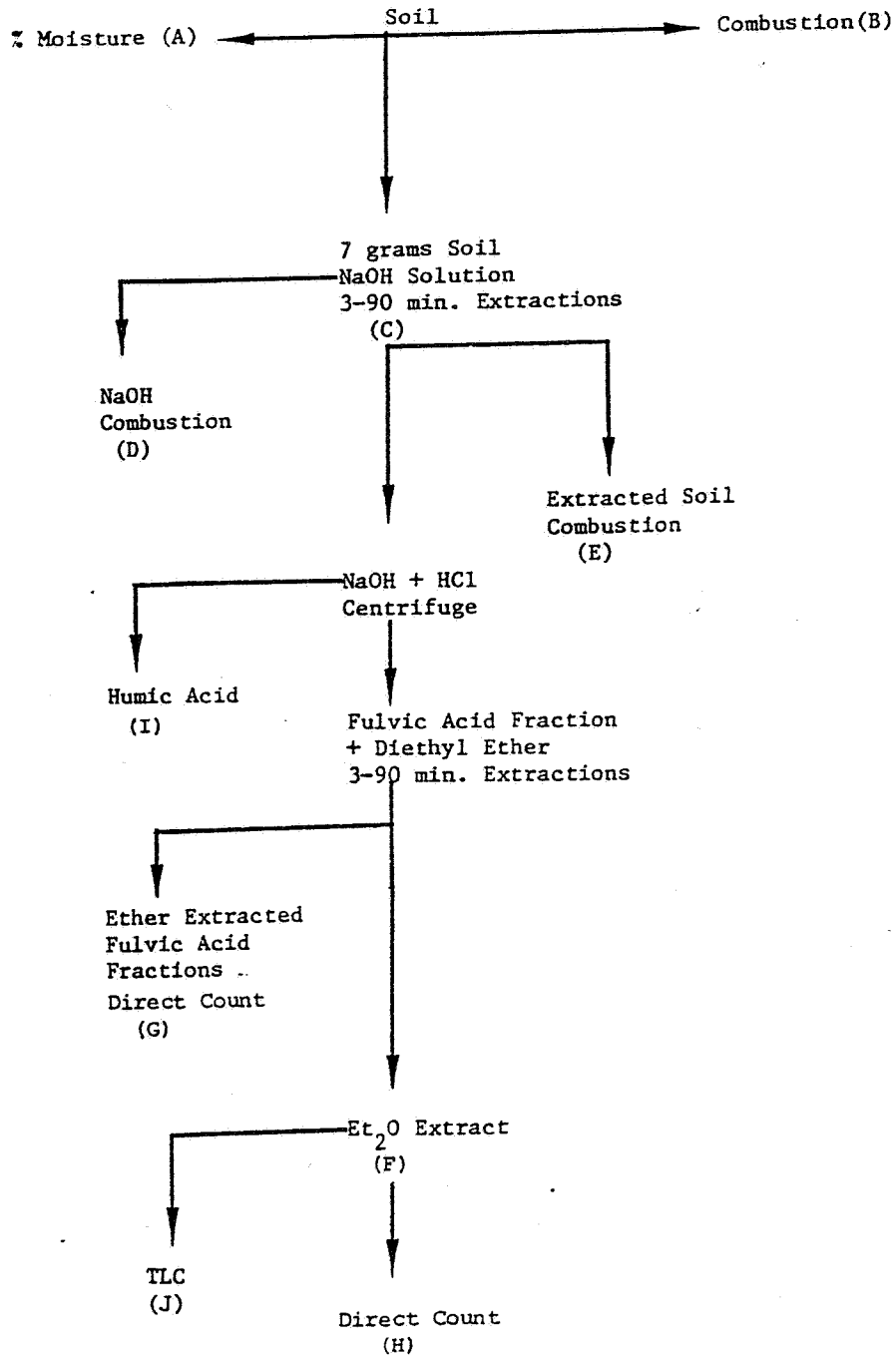
Procedure

¹⁴C-3,6-dichloropicolinic acid (labeled in the 2 and 6 positions) was added to 2 soils (Wayside soil of the Commerce series-23% 1/3 bar moisture, 28% sand, 52% silt, 20% clay, pH=6.6 and Geneso soil of the Flanagan series-26% 1/3 bar moisture, 20% sand, 52% silt, 28% clay, pH=5.2) to give a final soil concentration of 0.16 ppm.

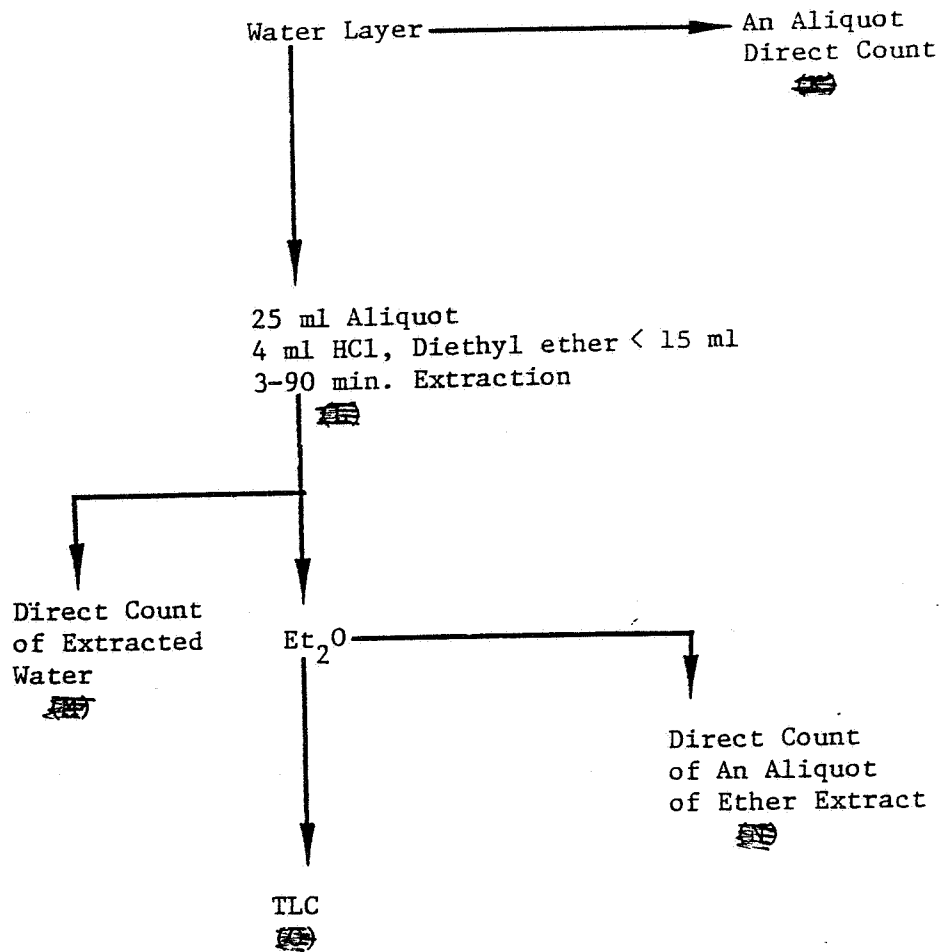
Samples from each soil were incubated under both aerobic, waterlogged and aerobic/waterlogged conditions (where waterlogging was done after 30 days of aerobic incubation).

Respired CO₂ was collected and the soil and water phases were analyzed for residues using standard extraction and radio-analytical techniques.

(FOR ANAEROBIC SAMPLES ONLY)



~~Flow Chart~~ FLOW CHART FOR SOIL ANALYSES



~~XXXXXXXXXX~~ FLOW CHART FOR WATER PHASE ANALYSIS FROM WATERLOGGED SAMPLE

2,4-D/Clorpryalid EFB review

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Conclusions

- 1) Degradation is more rapid under aerobic than under anaerobic conditions and is intermediate when anaerobicity is established after an aerobic period.
- 2) The Flanagan soil showed about 3X more CO₂ being released in the first month than did the Commerce soil (23.5 vs 61.7%). This greater degradation of parent compound may be due to a higher microbe population in the Flanagan soil as would be reflected by the higher organic matter content of the Flanagan soil. (The Flanagan soil would be expected to have 4% organic matter versus <1% for the Commerce soil).
- 3) Metabolites were not identified in this study.

- 3.10 Effect of 3,6-Dichloropicolinic Acid on Soil Microorganisms, P.J. McCall, Dow Chemical, November 29, 1979, GH-C 1260, acc. no. 099727, tab D.10

Comments

This data is not required at this time, according to the June 1981 draft of the Subpart N Guidelines. Therefore, it will not be reviewed in depth now.

The study, however, reports no negative effects on nitrification, nitrogen fixation, or on degradation of protein, starch cellulose and leaf litter at 1 ppm in the soil. Some studies were repeated at 10 ppm and still showed no negative effect.

- 3.11 Degradation of ¹⁴C-3,6-Dichloropicolinic Acid in Sterile and Non-Sterile Soils, R.L. Swann, et. Al., Dow Chemical, September 18, 1980, GH-C 1369, acc. no. 099727, tab no. D.11.

Procedure

Two soils, described below, were fortified to 0.25 ppm with ¹⁴C-3,6-dichloropicolinic acid (¹⁴C-labeled in the 2 and 6 positions). One sample of each soil was sterilized by auto-claving before fortification. The soils were brought to 75% of 1/3 bar, connected to a CO₂ trap and incubated in the dark at 25 °C.

2,4-D/Clorpryalid EFB review

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Conclusions

- 1) Microbial action is the major mode of degradation of DOWCO 290 in soil.
 - 2) Halflives of parent compound in the Commerce and Catlin soils were 62 and 12 days, respectively. No degradation products were identified.
- 3.12 The Influence of Soil Types on the Persistence and Leaching of DOWCO 290, S.D. Uprichard and A.J. Gilchrist, Dow Chemical, June 27, 1975, acc. 099727, tab D.12.

This study involved bioassay techniques which is not adequate for environmental fate determination.

- 3.13 Fate of 3,6-Dichloropicolinic Acid in Soils, Pik, et. al., J. Agric. Food Chem., Vol. 25, No. 5, 1977, acc. no. 099727, tab D.13.

Procedure

Several experiments were conducted to monitor the fate of 3,6-dichloropicolinic acid (DCP).

Overall disappearance - Three soils from Alberta, Canada, a black chernozem loam (17.8% sand, 71.7% silt, 10.5% clay, 4.8% OC, pH=7.7, field capacity=30.2%), a brown chernozem sandy loam (88.6% sand, 8.7% silt, 2.7% clay, 0.7% OC, pH=8.1, field capacity=21.3%) and an ortho eutric brunisol luvisol (40.8% sand, 47.2% silt, 10.5% clay, 1.3% OC, pH=7.2, field capacity=31.3%) were placed in clay pots 18 cm tall with drainage at the bottom and placed in the ground so the soil surface inside the pot was level with the surface of the ground. The pots were treated at 1.9 and 0.95 Kg/ha two weeks later and incorporated to 2 cm.

The experiment was carried out in 2 locations about 83 km apart in southwest Canada to see the effects, if any, of different climatic conditions.

Pots were periodically taken for analysis by the method of Pik and Hodgson, JAOAC. 59, 264 (1976).

Leaching study - Metal cylinders, 92 cm high by 19 cm in diameter were filled with 2 cm of gravel followed by 50 cm of soil. The same soils as described in the overall disappearance study above were used. A jar was connected to the bottom of the cylinder and the whole cylinder/jar set-up was placed in the ground such that the soil in the cylinder was level with the surface of the ground. After 2 weeks, the soil surface in the cylinder was treated at 0.95 kg/ha with DCP. After 9 weeks, the cylinders were removed and the soil sectioned into 4 segments of 12.5 cm each for analysis. Collected water was also analyzed.

Adsorption study - Adsorption coefficients (K_d) were determined by a soil column and a batch - type equilibrium method. The columns used were 31 cm long and of a 1.1 cm^2 cross-sectional area. They were filled with 2mm-sieved air-dried soil to 15 cm, pre-wet, and then treated at the top surface at 1.9 kg/ha. Leaching was initiated and continued under a constant head under an average flow rate of 0.5 ml/min until all of the DCP passed through the column. The eluate was extracted and analyzed by UV at 280 nm.

The batch-type method equilibrated 4 gm of soil with 4 ml of an aqueous 1.19 ppm solution of DCP for 10 hours at 21 °C. After centrifuging,

the supernatant was analyzed for DCP and the amount of DCP adsorbed was calculated by subtraction.

Degradation study - Jars (1.9 l) were filled with 1 kg of soil and 1.47 mg of DCP (1.9 kg/ha) were added. The jars were loosely capped and placed in the ground. The caps were removed for several minutes each week to renew the air in the jars. After 9 weeks, the soils were analyzed. The fact that the jars were capped may have promoted anerobic conditions.

A parallel experiment using sterilized soils was run with periodic analysis over 14 months.

In another experiment, 0.5 gm of black chernozem soil was added to 4 ml of a culture medium and 2 mg of DCP in a neutral aqueous was then added. The incubation tubes were shaken in a water bath at 25 °C. Samples were analyzed periodically by centrifuging and diluting 1 ml of the supernatant with 50 ml of water and analyzing under UV from 350 to 200 nm. Also, a sample from day 72 was analyzed for metabolites by extraction and EC-GC and GC-MS.

Results

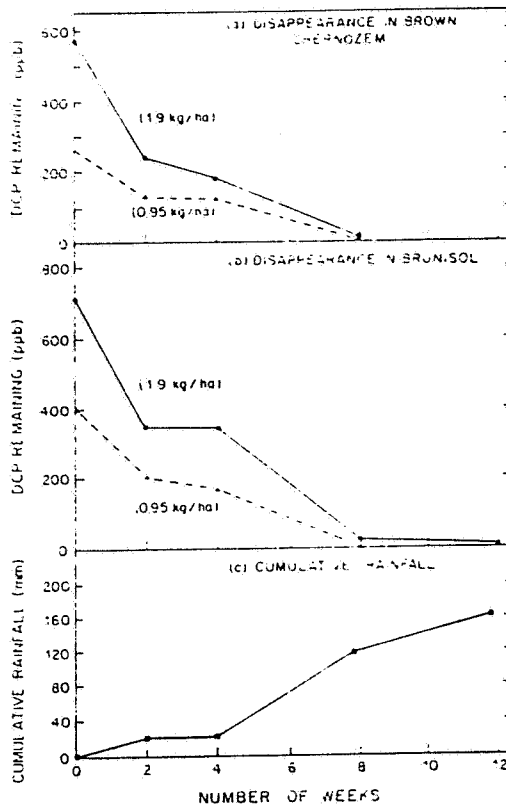


Figure 1. Disappearance rates of DCP in soils and cumulative rainfall at Kananaskis from July 4 to September 26, 1974. Initial application rates were at 1.9 and 0.95 kg/ha on both brown chernozem and brunisol as shown.

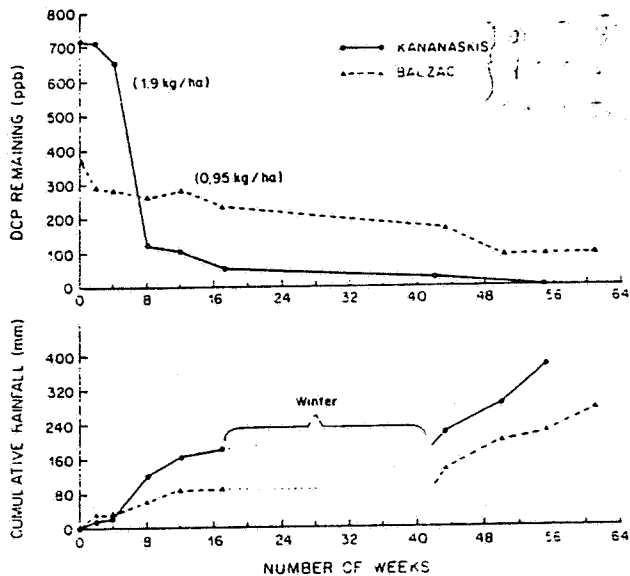


Figure 2. Disappearance rates of DCP in black chernozem and cumulative rainfall at Balzac and Kananaskis from July 4, 1974 to September 11, 1975. Initial application rates were 1.9 kg/ha at Kananaskis and 0.95 kg/ha at Balzac.

I Climatological Data for Kananaskis from July 8 to September 11, 1975, during which the Field Leaching Study Was Performed

Week	Rainfall, mm	Temperature, °C	
		Mean max.	Mean min.
1	21.1	25.0	10.5
2	2.0	20.0	9.7
3	37.6	25.0	9.7
4	5.1	16.8	6.5
5	2.5	18.9	4.1
6	32.0	17.9	6.0
7	6.6	16.8	4.7
8	6.6	16.2	4.8
9	2.5	18.9	1.7
Total	119.3	19.5 (Av)	6.4 (Av)

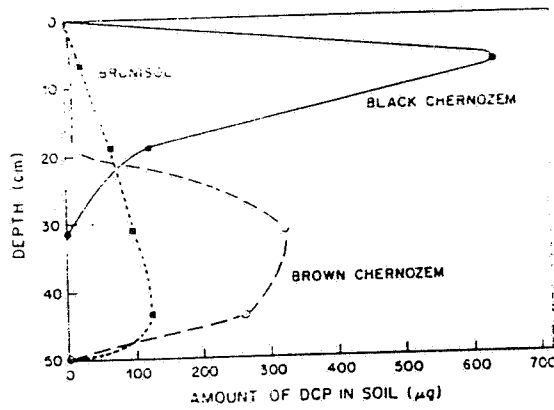
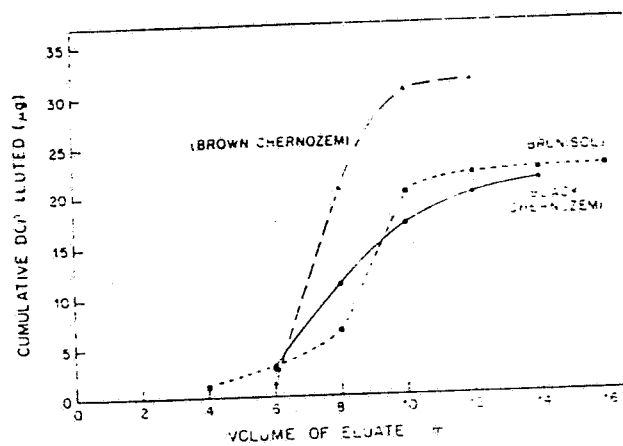


Figure 3. Concentration profiles of DCP remaining in soils after a period of 9 weeks during which 119 mm of rainfall occurred. The herbicide was applied on July 8, 1975 at the rate of 0.95 kg/ha. The three curves are arbitrarily extended to the zero concentration level at zero depth.



*In field application
0.95 kg/ha*

Figure 4. Elution curves of DCP from soil columns, 15 cm high and 0.7 cm in diameter. Application at 0.95 kg/ha. Flow rates averaged 0.5 ml/min.

Table II. Adsorption Equilibrium of DCP Expressed in Various Ways^a

Soil	Org. C content, %	Concentration on solid, $\mu\text{g/g}$	K_d , mL/g	Percent adsorp.
Black chernozem	4.8	0.12	0.10	9.6
Brown chernozem	0.68	0.01	0.01	0.8
Ortho eutric brunisol	1.3	0.05	0.04	4.1

^a Determined by batch-type equilibrations at 21 °C using a 1:1 soil/solution ratio at an original concentration of 1.19 ppm.

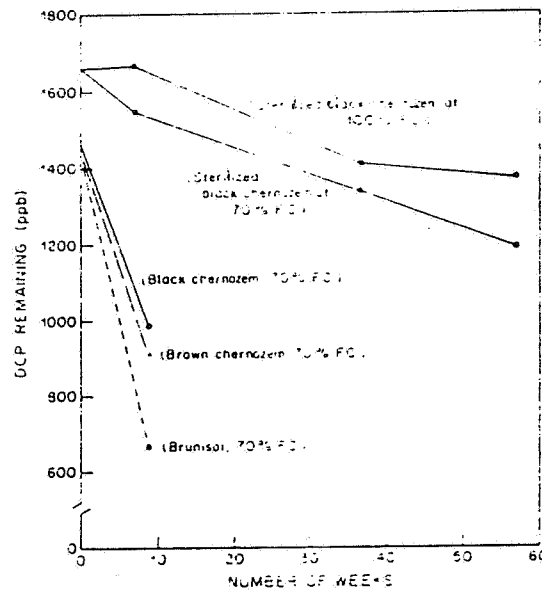


Figure 5. Degradation rates of DCP in natural and sterilized soils at Kananaskis. Initial application of the herbicide was 1.9 kg/ha.

Table III. Predicted and Experimental Depths of Leaching of DCP in Three Soils Occurring as the Result of a Total Rainfall of 119 mm in the Field at Kananaskis

Soil	Bulk density ρ , g/cm ³	Void ^a fraction, θ	Density of soil solids, d_s , g/cm ³	Experimental K_d		Observed ^c depth of leaching, cm	Calculated ^d depth of leaching, cm		Calculated ^e depth of leaching, cm	
				Column	Batch		Column	Batch	Column	Batch
Black chernozem	0.9	0.491	1.77	0.38	0.10	7	14.3	20.5	13.6	17.3
Brown chernozem	1.4	0.364	2.20	0.06	0.01	32	26.6	31.6	22.1	22.9
Ortho eutric brunisol	1.1	0.436	1.95	0.11	0.04	43	21.4	24.9	17.9	19.6

^a Void fraction, θ = void volume/soil volume. ^b Density of soil solids, $d_s = \rho / (1 - \theta)$. ^c Determined as the depth to maximum concentration, from the curves of Figure 4. ^d Depth of leaching, cm = $R / (\rho K_d + \theta)$, where R is total rainfall, 11.9 cm. ^e Depth of leaching, cm = $R / [\theta^{2/3} (1 - K_d d_s) + K_d d_s]$.

Conclusions

- 1) Greater dissipation (including leaching out of the test soil) was noted in the brown chernozem and in the brunisol than in the black chernozem. Half-lives of about 2 weeks, 2 weeks and 7 weeks, respectively, were found. The slower degradation of DCP in the black chernozem is noted at the 0.95 kg/ha fortification level and is coincident with a 50% lower rainfall. Soil degradation was slower in jars placed outdoors.
- 2) The leaching and adsorption data are in agreement in that high leaching and low adsorption were shown. However, the field leaching data show no leaching of parent compound beyond 50 cm. over a period of 9 weeks and 119.3 mm of accumulated rainfall. Although the method of analysis was only for parent compound, soil metabolism data show only 1 metabolite to form and only at levels not exceeding 10% of initial. The field leaching data also shows 45 - 77% of the initial parent compound to degrade over 9 weeks in the field.
- 3) Adsorption increased and leaching decreased with increasing organic carbon content. K_d values of 0.01 to 0.12 were found.
- 4) Degradation in sterilized soil was much slower than in non-sterile soil indicating microbial metabolism to be the major mode of soil degradation.
- 5) Slow degradation was seen in the soil enriched culture medium (15% after 96 days) and may be due to the fact that the soil microbes were exposed to 400 ppm DCP in the medium and could not adapt to that much DCP as quickly as they adapted to the 1-2 ppm concentrations in the soil disappearance and degradation studies.
- 6) Due to the high leachability of this chemical and the statement in this report "... the herbicide may pose problems in groundwater contamination.", field monitoring for leaching and possible groundwater contamination will be recommended as a condition for registration.

3.14 Determination of Residues of 3,6-Dichloropicolinic Acid (DOWCO 290) in Soil Cores from Leaching and Persistence Studies in the U.K. During 1974, E.M. Jones, Dow Chemical, November 10, 1975, acc. no. 099727, tab D.14.

Procedure

Outdoor plots (2 x 10 m) of a sandy loam soil were treated with an alkanolamine salt formulation of DOWCO 290 at 200 and 400 gm ai/ha. To determine extent of leaching, soil cores were taken to 18". The sandy loam was 80.6% sand, 17% silt + clay, 2.4% OM and pH = 7.2.

To determine persistence, a silty loam (55.5% sand, 43% silt + clay, 1.5% OM, pH = 7.9) was treated with DOWCO 290 at 48-100 gm ai/ha (in a tank mix with other chemicals) and sampled periodically to 9 inches.

The soil was analyzed for parent compound by aqueous basic extraction followed by acidification and partitioning into ether. The ether phase was methylated, cleaned and analyzed by EC-GC for the methyl ester of 3,6-dichloropicolinic acid.

Rainfall and temperature data were not included.

Conclusions

- 1) Although the data show no detectable leaching beyond 18 inches, the lack of rainfall data do not allow an assessment of the leaching potential.
- 2) The potential for field dissipation cannot be determined because only 1 sample (112 days after application) was taken and rainfall and temperature data were not submitted.
- 3) These studies were not conducted on U.S. agricultural soils which makes the data of limited utility.

3.15 Residues of 3,6-Dichloropicolinic Acid and 2,4-Dichlorophenoxyacetic Acid in Soil Treated with LONTREL 205 Herbicide, R.D. Glas, GH-C 924, Dow Chemical, August 10, 1976, acc no. 099727, tab D.15.

Procedure

Wheat and barley plots were treated with 3,6-DCP at 4 oz ai/A and 2,4-D at 16 oz ai/A for 2 consecutive years. Soil cores were taken to 24 inches during the year following the first application and up to 14 weeks following the second application.

Soil samples were analyzed by acidifying and extracting with ether. The ether extract was partitioned with sodium bicarbonate solution. The bicarbonate was acidified, extracted with ether, esterified with diazomethane, cleaned, evaporated and taken up with hexane for analysis by EC-GC.

Rainfall data was included.

TABLE I. SOIL CHARACTERISTICS BY LOCATION

Location	Soil Series	% Organic Matter	pH	% Sand	% Silt	% Clay
Davis, CA	Yolo silt loam	1.7	7.1	20	61	19
Fargo, N.D.	Fargo clay	6	7.0	10	36	54
Pendleton, OR	Walla Walla loam	2.3	6.1	21	60	19
Corvallis, OR	Woodbury clay loam	3.2	5.2	15	52	33
Bozeman, MT	Bozeman silt loam	2.2	2.7*	19	50	31

*questionable value

Results

1) Residues (average) Found at Weeks Post-Treatment

Soil	Soil Depth inches	0	1	2	4	8	14	16	42	45	48	52	53	Second appl. made	12*	14*
Yolo	0-6	0.07		0.09	0.07	0.08		0.10	0.006				ND			
	6-12			ND	ND	ND		<0.005	<0.005				ND			
	12-18				ND	ND		ND								
	18-24							ND								
Fargo	0-6	0.04	0.04	0.07	0.04	0.01		ND				ND			<0.005	
	6-12			ND	ND	<0.005		ND				ND			ND	
	12-18			ND	ND	ND						ND			ND	
	18-24					ND						ND				
Walla Walla	0-6	0.009	0.01	0.01	0.01	0.02		0.02								0.005
	6-12			0.001	ND	ND		<0.005		ND						ND
	12-18			0.001	ND	ND		<0.005		ND						ND
	18-24							<0.005								
Woodbury	0-6	0.014	0.009	-	0.03	0.02										0.01
	6-12		0.010	0.006	0.01	0.02		<0.005								<0.005
	12-18			-	<0.005	<0.005		ND								ND
	18-24				ND	<0.005		ND								ND
Bozeman	0-6	0.06	0.05	0.14	0.10	0.07		0.07							0.006	
	6-12		0.01	0.02	0.03	<0.005		0.06			<0.005				0.005	
	12-18			<0.005	0.008	<0.005		0.03			ND					
	18-24					<0.005		0.03			ND				ND	

* Weeks after 2nd application

Conclusions

- 1) Halflives in the field were reached in 4-11 months depending on the soil.
 - 2) Leaching beyond 18 inches was not detected.
 - 3) Data are insufficient to determine if repeated yearly applications will result in soil residue build-up.
- 3.16 Soil Persistence and Accumulation of M-3785, R.E. Whitesides et. al., Oregon State University, April 26, 1976, acc. no. 099727, tab D.16.

Comments

This study involved detection of soil residues via bioassay techniques and not via chemical analysis. Therefore, this study is not germane to the Environmental Fate Branch.

- 3.17 A Rotational Crop Study Following the Application of DOWCO 290 to Spring Wheat, W.R. Bauriedel et. al., Dow Chemical, April 22, 1976, acc. no. 099727, tab D.17.

Prodedure

Five small plots of wheat at the full tillering stage were treated with M-3785 (a mixture of DOWCO 290 and 2,4-D) at the rate of 2 ounces DOWCO 290 (as the ai) per acre in 1973. In April 1974, wheat, soybeans and sugarbeets were planted as rotational crops.

Soil was sampled and analyzed for ^{14}C activity at harvest of the initial wheat crop and at planting of the rotational crops.

The mature wheat was harvested 95 days after planting. The soybeans and sugar beets were harvested 132 and 135 days after planting, respectively. Sugar beets were also harvested at mid-season.

^{14}C -Labeled DOWCO 290 was used but the site of radiolabeling was not specified in this report. Also, the exact dates of treatment and planting of rotational crops are not given.

The results of the soil analyses are in report GH-C 742 which was referenced by not submitted.

ResultsRadioassay of Rotational Crops

<u>Crop Sample</u>	<u>¹⁴C-Residue (ppm) as parent</u>
Wheat - grain	<0.01
- straw	<0.01
Sugarbeets - mid-season	<0.01
Sugarbeets - roots	<0.01
- tops	<0.01
Soybean - beans	<0.01
- vines	<0.01

Conclusions

This study cannot be fully evaluated without (1) a copy of report GH-C 742, (2) specifying the site of radiolabeling, (3) providing the exact dates of pesticide treatment and planting of rotational crops, (4) providing the characteristics of the soil and (5) a record of daily temperature and accumulated rainfall.

4. CONCLUSIONS

- 4.1 The new active ingredient, 3,6-dichloropicolinic acid (DCP) will be stable to hydrolytic and aqueous and soil surface photolytic conditions that would occur in the environment.
- 4.2 The laboratory soil half-life of DCP at 25 °C was 1-2 months in most soils tested but did jump to 6-10 months in a few soils. This range in half-lives is probably due to microbial adaptation. Ring cleavage is extensive with the release of CO₂ and only one soil metabolite, 3-chloro-6 hydroxypicolinic acid, is found and at small amounts (<10% of initial). A change in fortification levels from 0.25 to 1.0 ppm is reflected in the half-life being increased by a factor of 2-3X. Soil degradation is also very dependant on soil moisture and temperature. This information, coupled with the fact that DCP persists in sterile soil, indicates the major mode of soil degradation to be microbial. The half-life of DCP under anaerobic soil conditions is greater than 10 months.
- 4.3 Unclear data have been submitted by the registrant which do not allow a firm assessment of the leaching potential of DCP.

Data submitted indicating high leaching potential are DCP's high water solubility (10-25%), low soil adsorption K_d values of 0.01-0.12, the high amount of acreage proposed and the statement in the J. Ag. Food Chem. article submitted by the registrant that "... the herbicide may pose problems in groundwater contamination." The low proposed rates of application of 1/16 - 1/8 lb ai/A, however, temper the above data.

There is data, though, that appear to show no leaching but need additional information before a final conclusion that no leaching will occur can be made. For example a field column leaching study (section 3.13) showed no leaching beyond 50 cm over 9 weeks and 119 mm of rainfall but anaerobic conditions were probably not experienced by the chemical at depths near 50 cm due to the soil being disturbed in setting up the experiment. Under use conditions, anaerobic conditions would be encountered at depths less than 50 cm thereby prolonging the soil life of DCP and allowing leaching of residues to greater depths. The leaching data from the U.K. (section 3.14), showing no leaching beyond 18 inches is of limited utility because the study did not employ a U.S. agricultural soil common to the proposed use areas and did not supply rainfall data. A U.S. study (section 3.15) conducted under use conditions showed no detectable leaching beyond 18 inches but the possibility of residue build-up due to repeat applications and subsequent leaching cannot be adequately addressed. Also, the studies using bioassay methods are not acceptable to EFB due to inherent limitations in bioassay methods (see section 3.8)

Due to the unclear nature of the leaching data, field monitoring for leaching and groundwater contamination under use conditions over 3 consecutive seasons is recommended.

- 4.4 The microbial data is not required at this time and therefore was not reviewed. See section 3.10.
- 4.5 The field dissipation data on Canadian soil (section 3.13) and on U.K. soils (section 3.14) are of limited utility because U.S. agricultural soils common to the proposed use areas were not used. See section 4.3, above. The study run on the U.S. soils (section 3.15) showed a half-life of DCP of 4-10 months with no leaching detected beyond 18 inches. However, whether residue buildup from repeat applications with subsequent leaching of those residues will occur cannot be adequately addressed from the study as too few samples were taken. This information can be derived from the recommended field monitoring study at the end of 4.3 above.
- 4.6 A flow-through fish accumulation study was not submitted and is needed especially in light of the relatively high water solubility of DCP, its possible soil persistence and the large acreage in the proposed use areas.

- 4.7 The rotational crop data cannot be fully evaluated without additional information. See the conclusions of section 3.17 and section 5.1.2, below.
- 4.8 Other comments on the data appear in the RECOMMENDATIONS section below.

5. RECOMMENDATIONS

- 5.1 We do not concur with registration. The following data requirements were not or were not adequately addressed:
- 5.1.1 A flow-through fish accumulation study has not been submitted and is needed.
- 5.1.2 The rotational crop study cannot be fully evaluated without (1) a copy of GH-C 742, (2) specifying the site of radiolabeling, (3) providing the exact dates of pesticide treatment and planting of rotational crops (4) providing the characteristics of the soil and (5) a record of daily temperature and accumulated rainfall.
- 5.1.3 The leaching and field dissipation data do not allow a clear assessment of leaching potential. A field study monitoring for leaching, possible groundwater contamination and field dissipation over 3 consecutive seasons of DCP use will be needed as a condition of registration and will not be needed prior to the granting of registration. Data are to be generated under use conditions with submission of results every 6 months. If leaching and/or groundwater contamination is found, the conditional registration may be cancelled. It is suggested that protocol for the field study be submitted for comment by EFB before initiating the study.
- 5.2 The following comments refer to specific items or reports.
- 5.2.1 Is only one application of LONTREL to be made per year?
- 5.2.2 In study GH-C 910, reviewed in section 3.4 above, results for soils S₃, S₄ and S₅ are missing. Also, please explain how the half-life for soil S₁ of 24 days was derived.
- 5.2.3 In study GH-C 1333, please explain how the half-life for the Fargo soil in Table III was derived.
- 5.2.4 Please indicate the organic matter content of the soils used in study GH-C 965. Also, verify the pH of the Bozeman soil in study GH-C 924.

Samuel M. Creeger July 27, 1981

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 July 27, 1981
 Section #1
 Environmental Fate Branch/HED