Shaughnessy No.: 128201

Date Out of EAB: DEC 23 1985

To: R. Taylor
Product Manager 25
Registration Division (TS-767)

From: Emil Regelman, Chief (acting)
Review Section #3
Exposure Assessment Branch
Hazard Evaluation Division (TS-769)

Attached, please find the EAB review of...

Reg./File # : 352-UUR

Chemical Name: DPX-Y6202

Type Product : Herbicide

Product Name : Assure

Company Name : du Pont

Purpose : Registration on cotton and soybeans

Action Code(s): 110

Date Received: 6/12/85

Date Completed: DEC 23 1985

EAB #(s) : 5669

TAIS Code: 301

Total Reviewing Time: 10.0 days

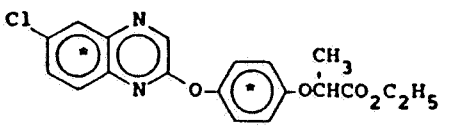
Deferrals to:

____ Ecological Effects Branch

____ Residue Chemistry Branch

____ Toxicology Branch

1. Chemical: DPX-Y6202 or NC-302 duPont Assure



DPX-Y6202

Ethyl 2-[4-(6-chloroquinoxalin-2-yloxy)phenoxy]propanoate

2. Test Material:

Study 1. phenyl-[^{14}C]-DPX-Y6202 65 uCi/mg $\geq$ 99.3% purity.
quinoxaline-[^{14}C]-DPX-Y6202 58 uCi/mg $\geq$ 99.3% purity.

Study 2. phenyl-[^{14}C]-NC-302 8.5 uCi/m mol >99% purity.

Study 3. phenyl-[^{14}C]-DPX-Y6202 19.3 uCi/mg $\geq$ 99.3% purity.

Study 4. phenyl-[^{14}C]-NC-302 8.3 uCi/m mol 99% purity.
quinoxaline-[^{14}C]-DPX-Y6202 7.8 uCi/m mol 98% purity.

Study 5. phenyl-[^{14}C]-DPX-Y6202 65 uCi/mg 99% purity.
quinoxaline-[^{14}C]-DPX-Y6202 19.3 uCi/mg 99% purity.

Study 6. quinoxaline-[^{14}C]-DPX-Y6202 58 uCi/mg $\geq$ 99.3% purity.

Study 7. phenyl-[^{14}C]-NC-302 8.5 uCi/m mol 99% purity.
phenyl-[^{14}C]-NC-302 acid 8.5 uCi/m mol 97% purity.

Study 8. phenyl-[^{14}C]-NC-302 8.5 uCi/m mol 99% purity.
phenyl-[^{14}C]-NC-302 acid 8.5 uCi/m mol 97% purity.

3. STUDY/ACTION TYPE:

Data for registration of DPX-Y6202 on cotton and soybeans.

Study 1. Photodegradation in water.

Study 2. Photodegradation in soil.

Study 3. Aerobic soil metabolism.

Study 4. Aerobic and anaerobic soil metabolism.

Study 5. Anaerobic soil metabolism.

Study 6. Leaching and adsorption/desorption.

Study 7. Leaching and adsorption/desorption.

Study 8. Adsorption/desorption.

4. STUDY IDENTIFICATION:

All studies in:

Pesticide Petition for tolerance for du Pont Assure® Herbicide in or on cotton or soybeans. Volume 20 Section D2 Environmental Fate Data. Accession # 073548.

1. Ryan, D.L. 1985. Photolysis of DPX-Y6202 in water. E.I. duPont de Nemours and Co. Inc. Agricultural Chemicals Dept., Research Div. Experimental Station, Wilmington DE 19898. Report No. AMR-275-84 exhibit 44.

2. Wakabayashi, T., H. Hirata, and S. Takano. 1985. Photolysis of NC-302 on soil. Nissan Chemical Industries Ltd. Copyright by E.I. duPont de Nemours and Co. Inc. exhibit 45.

3. Cadwgan, G.E. and R.D. McFetridge. 1985. Aerobic soil metabolism of [Phenyl-^{14}C(U)] DPX-Y6202. E.I. duPont de Nemours and Co. Inc. Agricultural Chemicals Div., Wilmington DE Report No. AMR-329-85 exhibit 46.

4. Hirata, H., T. Wakabayashi, S. Takano, I. Yamaguchi and T. Misato. 1985. Degradation of NC-302 in soil. Nissan Chemical Industries Ltd. Copyright by E.I. duPont de Nemours and Co. Inc. exhibit 47.

5. Cadwgan, G.E., R.D. McFetridge. 1985. Anaerobic aquatic soil metabolism of [Quinoxaline-[^{14}C]-DPX-Y6202 and [Phenyl-^{14}C (u)]-DPX-Y6202. . E.I. duPont de Nemours and Co. Inc. Agricultural Chemicals Division, Wilmington DE. Report No. AMR-350-85. exhibit 48.

6. Priester, T. 1985. Batch equilibrium (adsortion/desorption) and soil thin-layer chromatography studies with [quinoxaline-phenyl-^{14}C(U)]-DPX-Y6202. E.I. duPont de Nemours and Co. Inc. Agricultural Chemicals Department, Research Division Experimental Station Wilmington DE. Report No. AMR-314-85. exhibit 49.

7. Wakabayashi, T., H. Hirata and S. Takano. 1985. Mobility of NC-302 in soil. Nissan Chemical Industries, Ltd. Copyright E.I. duPont de Nemours & Co. exhibit 50.

8. Wakabayashi,T., H. Hirata and S.Takano. 1985. Soil adsorption and desorption of NC-302 in soil. Nissan Chemicals Industries, Ltd. Copyright E.I. duPont de Nemours & Co. exhibit 51.

5. REVIEWED BY:

Paul Mastradone
Chemist
EAB/HED/OPP

Signature: Paul J Mastradone

Date: 12/23/85

6. APPROVED BY:

Emil Regelman
Acting Chief
Review Section #3,
EAB/HED/OPP

Signature: E Regelman

Date: DEC 23 1985

7. CONCLUSIONS:

There are insufficient data to support the registration of DPX-Y6202. This submission contained the following studies:

Study 1. Photodegradation in water: Scientifically valid study which fulfilled guidelines. Study indicates DPX-Y6202 undergoes aqueous photodecomposition (peak wavelength 376 nm, pH 5, 25°C) with a half-life of 55 days. Major decomposition products were successfully identified and materials balance provided. Major degradates reported to be DPX-acid, phenol-1 and phenol-2 degradates. Major pathway for decomposition was via CO_2. No additional data will be required.

Study 2. Photodegradation in soil: Scientifically valid study that does not fulfill guidelines as the soils used were foreign with no comparison made to U.S. soils and all metabolites formed in excess of 0.01 ppm were not identified, and only monochromatic light (365 nm) was used. Photolysis at 365 nm resulted in a $t_{1/2}$ of 30 days. Major pathway of elimination was found to be similar to that reported in aqueous solution (via CO_2 formation).

Study 3. Aerobic soil metabolism: Scientifically valid study that fulfilled guidelines and described the aerobic degradation of DPX-Y6202 in a sandy loam and silt loam soil. Study included a materials balance, a half-life estimate of about 1 day and a description of the major degradates formed. The major pathway of elimination was mineralization of the phenyl ring to CO_2 which occurred after 10 or more weeks of aging. Additional data will be necessary only if use patterns indicate that soils other than silt loams or clay loams are to be use sites.

Study 4. Studies were scientifically invalid because the methods and data were incompletely reported. Additionally the studies did not meet guidelines as they were done on foreign soils with no U.S. soil equivelant.

Aerobic soil metabolism: In addition to the above described deficiencies this study failed to meet guidelines because no incubation temperature was reported, no attempts were made to insure aerobic conditions were maintained, and no decline curves were provided.

Anaerobic soil metabolism: Study failed to meet guidelines for above described reasons. Additionally, the soils were not aged aerobically for 30 days after addition of test substance prior to initiation of anaerobic conditions.

Study 5. Anaerobic aquatic metabolism: Scientifically valid study that failed to meet guidelines because all metabolites in concentrations greater than 0.01ppm were not identified. Anaerobic metabolism to DPX-acid was rapid with a half-life of 1 day. Further metabolism is to phenols 1,2,4 and hydroxy-phenol-2 with respective half-lives of 6 and 13 weeks.

Study 6. Leaching and adsorption/desorption: Scientifically valid batch equilibrium study that partially meets guidelines as the mobility of the major degradates of DPX-Y6202 was not established. DPX-Y6202 was classified as class 1 (immobile) by soil TLC.

Study 7. Leaching and adsorption/desorption: Scientifically valid soil mobility/TLC study which did not fulfill guidelines as the study was done on foreign soils with no U.S. equivalent. Study identified the mobility of DPX-Y6202 and DPX-acid only and not the mobility of any of the other major degradates. DPX-Y6202 was classified as immobile and DPX-acid was classified as low mobility.

Study 8. Adsorption/desorption: Scientifically valid study that did not fulfill guidelines because the soils used were foreign with no comparison to a U.S. equivalent. On the test soils DPX-Y6202 was classified as immobile and DPX-acid, a major degradate, classified as slightly mobile. Study compared the mobility of DPX and DPX-acid to the mobility of DDT and 2,4-D. Results indicate that the absorptivity order is DDT>DPX>DPX-acid>2,4D .

In summary there are not sufficient data available at this time to support the registration of DPX-Y6202. To date, the registant has filled only the hydrolysis, photodegradation in water, aerobic soil metabolism and fish accumulation requirements for registration.

Data are still inadequate to support an EUP as to date no acceptable leaching or rotational crop data have been submitted.

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8. RECOMMENDATIONS:

For all studies which used foreign soils, the registrant should submit data comparing these soils to a U.S. equivalent. If this data cannot be provided the registrant must repeat the studies on U.S. soils. In addition:

Photodegradation in soils (161-3): Submitted study did not fulfill data requirements as previously noted. Additionally, each metabolite produced in 10% or greater yield must be identified. If this data cannot be provided a new study must be submitted to fulfill this data requirement.

Anaerobic soil metabolism (162-2): Study did not fulfill guidelines as noted. A new study will be needed. Data to fulfill this requirement need not be submitted if the anaerobic aquatic metabolism data requirement is successfully filled.

Anaerobic aquatic metabolism (162-3): Guidelines require the identification of all metabolites occurring in >0.01ppm concentrations. The registrant should be instructed to identify those metabolites that occurred at greater than this concentration. If this data cannot be provided a new study will be necessary.

Leaching and adsorption/desorption (163-1): Since complete leaching data is not available for parent DPX-Y6202 or degradates on representitive soils EAB suggests that a new study be done. This study should be done on U.S. soils and selected as described in section 163-1 section (C) (2) (iii) of the guidelines. The leaching potential of DPX-Y6202 and all degradates should be described in this study.

9. BACKGROUND:

The registrant has requested an EUP on several occasions and each time this request has been denied as it lacked supporting data. In review the following data requirements have been filled in previous submissions:

Hydrolysis: An acceptable hydrolysis study has been submitted. Reported half-lives were 2days @ pH9, 30 days @ pH7 and >600 days @ pH 5. The major degradate was reported to be the deesterified acid of DPX-Y6202. Review date 1/26/84.

Accumulation in fish: An acceptable study was submitted stating that total bioaccumulation of DPX-Y6202 in the edible portions of mussels was 16x and 10x on days 1 and 7 for two aqueous concentrations. The 28 day values were 1x and 4x with a 14 day depuration value of 0.3x Review date was 1/26/84.

Several aerobic soil metabolism studies were submitted in the past. None have been found acceptable.

A rotational crop study was submitted in support of an EUP on cotton and soybeans but was found unacceptable. Reviews of 9/17/84 and 8/23/85.

10. DISCUSSION:

Discussion of the individual studies can be found in the attached Dynamac review. This report was reviewed, corrected and approved by EAB.

11. COMPLETION OF ONE-LINER:

One-liner not updated at this time.

12. CBI APPENDIX:

The apppended report contains data which the registrant may consider as CBI and should be treated as such.

DYNAMAC
CORPORATION

DPX-Y6202

Final Report

Task 1: Review and Evaluation of Individual Studies

Task 2: Environmental Fate and Exposure Assessment

Contract No. 68-01-6679

SEPTEMBER 18, 1985

Submitted to:
Environmental Protection Agency
Arlington, VA 22202

Submitted by:
Dynamac Corporation
Enviro Control Division
The Dynamac Building
11140 Rockville Pike
Rockville, MD 20852

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This report is a scientific evaluation of environmental fate data submitted under Accession No. 073548. In addition to the eight studies reviewed herein several studies reviewed previously (not by Dynamac) are contained in the EAB files. The contribution of these studies to the fulfillment of EPA Requirements for Pesticide Registration is considered under Recommendations.

Diagrams of chemical structures included in this report have not been redrawn by the reviewer. Other figures are photocopies of submitted materials. Tables have been retyped and in many instances reformated. Data not directly reported by the registrant (i.e., data calculated by the reviewer) are indicated as such either in tables or in the text.

DPX-Y6202
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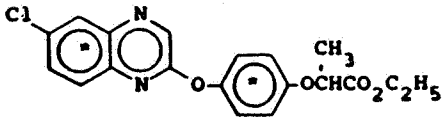
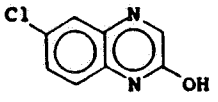


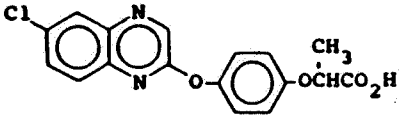
DPX-Y6202

Ethyl 2-[4-(6-chloroquinoxalin-2-yloxy)phenoxy]propanoate



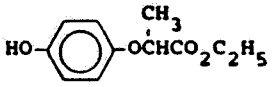
"Phenol 2"

6-chloroquinoxalin-2-ol



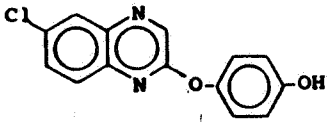
"DPX-Y6202 Acid"

2-[4-(6-chloroquinoxalin-2-yloxy)phenoxy]propanoic acid



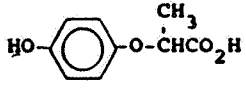
"Phenol 3"

ethyl-2-[(4-hydroxy phenyl)oxy]propanate



"Phenol 1"

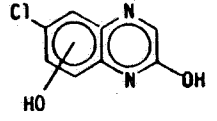
4-(6-chloroquinoxalin-2-yloxy)phenol



"Phenol 4"

2-[(4-hydroxyphenyl)oxy]propanoic acid

* (uniformly labeled on either the quinoxaline-phenyl or phenyl ring)



Hydroxy-Phenol 2

Hydroxylated 6-chloroquinoxaline-2-ol

CHEMICAL STRUCTURES AND NAMES FOR DPX-Y6202 AND POTENTIAL DECOMPOSITION PRODUCTS.

STUDY 1

Ryan, D.L., May, 1985. Photolysis of DPX-Y6202 in water. E.I. duPont de Nemours and Co., Inc. Agricultural Chemicals Dept., Research Div., Experimental Station, Wilmington, Delaware, 19898. Report No. AMR-275-84. Acc. No. 073548. Ref. Vol. 20, Sec. D2, exhibit 44.

Procedure

Samples of an aqueous buffer solution (sodium acetate/acetic acid) at pH 5, in flasks equipped with a side arm were autoclaved at 250°C (15-17 psi). These buffer solutions were fortified with phenyl-[C^{14}]-DPX-Y6202 (65 µCi/mg) and quinoxaline-[^{14}C]-DPX-Y6202 (58 µCi/mg) at 0.05 ppm and maintained at 25°C. A small air stream was drawn continuously into the flasks and passed through a gas washing bottle which contained sodium hydroxide.

The solutions were irradiated alternatively with fluorescent sunlamps and black lamps continuously for 28 days. The flasks and base-traps were sampled after 0, 2, 4, 7, 14, 22 and 28 days.

Methodology

At different intervals samples from the flasks and traps were radioassayed (LSC). $^{14}CO_2$ in the traps was confirmed by the precipitation of $Ba^{14}CO_3$ following the addition of saturated $BaCl_2$.

Photolyzed samples were extracted 4-5 times with methylene chloride:methyl ethyl:ketone (3:2 v/v) after acidification (HCl). Combined extracts were concentrated (roto-evaporator) and radioassayed (LSC). The aqueous phase was also radioassayed and the percent radioactivity in each fraction was determined based on [^{14}C]-DPX-Y6202 activity at time 0.

TLC analysis of the concentrated organic extract was carried out using Whatman plates eluted with toluene:ethyl ether:formic acid (55:45:2:5 v/v/v). Nonradioactive DPX-Y6202 and reference compounds were located by UV fluorescence quenching, and radioactive materials by autoradiography. Quantification was by integration of peak areas using a TLC linear analyzer.

Results

Aqueous photolysis of DPX-Y6202 was carried out at pH 5 since this compound readily hydrolyzed at pH 7 (half-life ~30 days) and pH 9 (half-life ~1 day)(1). Approximately 64% of the parent was recoverable after 28 days of irradiation (Table 1) at a wavelength of 376 nm which was close to summer sunlight. The estimated half-life of DPX-Y6202 was 55 days based on a plot of recovery data with time.

DPX-Y6202 decomposition products present in the organic phase and tentatively identified were:2-[4-(6-chloroquinoxaline-2-yloxy)-phenoxy]-propanoic acid (DPX-acid), 4(6-chloroquinoxaline-2-yloxy)-phenol (phenol-1) and 6-chloroquinoxaline-2-ol-(phenol-2) (Figure 1). Both phenols-1 and 2 were present in the quinoxaline-labeled samples but only phenol-1 was present among the phenyl-labeled photoproduct. All three products were less than 5% of total recovered radioactivity.

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Approximately 6% of measured radioactivity were unextractable polar unknowns which remained in the aqueous phase. Non-polar unknowns were present in the organic extract with both labels and reached a high of 11% of applied ^{14}C activity. 8-9% of original radioactivity was recoverable as $^{14}CO_2$ from the sodium hydroxide trap after 28 days.

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Table 1. Aqueous photodegradation of DPX-Y6202 at 376 nm and 0.05 ppm.

Irradiation Time (days)	% ^{14}C recovered*								
	Phenyl-[^{14}C]-DPX-Y6202								
	Organic	H_2O	CO_2	DPX-Y6202	Phenol 1	Phenol 2	DPX-Acid	a	b
0	89	0	0	88	0.1	--	0.4	0	0.1
2	98	0.7	0.4						
4	85	1.6	0.7	74	2.3	--	2.3	4.5	2.0
7	90	2.3	1.6	79	0.7	--	0.9	6.8	3.2
14	88	3.9	3.6	67	2.4	--	3.6	11	3.9
22	91	4.9	7.1	71	1.8	--	4.0	9.9	4.8
28	84	5.7	9.3	64	3.4	--	4.0	8.5	3.7
	quinoxaline-[^{14}C]-DPX-Y6202								
0	88	0	0	87	0.4	0.6	0	0.4	0.3
2	95	0.2	0.6	89	0.9	0.8	0.2	2.1	1.7
4	96	0.7	1.3	90	0.9	1.3	0.3	1.7	1.7
7	92	2.2	2.1	81	2.4	0.9	1.3	4.8	1.7
14	98	1.6	4.0	78	3.1	3.2	2.5	6.8	4.4
22	95	3.2	6.5	74	3.8	3.0	2.7	4.8	6.6
28	90	3.0	8.0	67	5.1	4.1	1.5	3.4	8.2

* Radioactivity of DPX-Y6202 at time 0 assumed to be 100%.

a Non-polar unknowns with R_f >0.05

b Non-polar unknowns with R_f <0.05

Conclusions

DPX-Y6202 undergoes aqueous photodecomposition at 376 nm (pH 5, 25°C) with a reported half-life of 55 days. Three major decomposition products were tentatively identified by comparison of R_f values of unknowns with reference materials. Material balances were provided for this reaction which included both polar and nonpolar unknowns, the individual concentrations of which never exceeded 5%. The major photodecomposition pathway involved the elimination of CO_2 from DPX-Y6202.

STUDY 2

Wakabayashi, T., Hirata, H., Takano, S. February, 1985. Photolysis of NC-302 on Soil. Nissan Chemical Industries, Ltd. Copyright by E.I. du Pont de Nemours and Co. Acc. No. 073548 Ref. Vol. 20, Sec. D2, exhibit 45.

Procedure

Sieved Chiba soil (silty loam, pH 6, organic matter 5.1%) was added to thin layer plates. The soil thin layer plates were treated uniformly (0.4 $\mu g/cm^2$) with [^{14}C]-phenyl-NC-302 (8.5 mCi/m mol, >99% pure). After drying at room temperature the plates were irradiated at 25-30°C with UV light (high pressure mercury vapor, 365 nm) in a flask with a side arm. A stream of air was passed continuously through the flask during irradiation into an organic matter trap (toluene) and a CO_2 trap (NaOH). Soil plates and traps were sampled after 0, 3, 7, 14, and 30 days. A dark control study followed the same procedure only the soil plate was kept in the dark and not irradiated.

Methodology

At each sampling interval, the soil was scrapped from the plate and extracted first with acetone:phosphoric acid (4:1) then methanol:Phosphoric acid (4:1). The organic extracts were radioassayed (LSC) and the residual soil was combusted (O_2) and unextractable radioactivity determined as $^{14}CO_2$ by LSC.

TLC analysis of the organic extracts was carried out using silica gel plates eluted with ether:hexane:acetic acid (10:10:0.3), benzene:ethyl acetate:acetic acid (4:2:1) or (16:8:1). Non-radioactive NC-302 (DPX-Y6202) and reference compounds were detected by UV quenching and radioactive materials by autoradiography.

The presence of CO_2 in the base-traps was confirmed by the addition of HCL. It was assumed, not stated, that $^{14}CO_2$ in the traps were quantified by LSC.

Results

Soil thin-layer photolysis of DPX-Y6202 resulted in approximately 50% of the parent being recoverable after 30 days of irradiation (Table 2) at 365 nm. The estimated photo half-life of DPX-Y6202 would then be 30 days if first order kinetics was assumed. Most of this decomposition occurred within the first three days of exposure.

DPX-Y6202 decomposition products identified from the organic phase were "DPX-acid", phenol-1 and phenol-3. No phenol-2 was reported or expected since only phenyl-labeled material was used (Figure 1, Study 1). All four products were less than 5% of total recovered raioactivity (Table 2). Most of the applied radioactivity was extractable from the dark control after 30 days of storage. This indicated that the decomposition which occurred with the exposed plate was photo-induced.

17% of original radioactivity was recoverable as $^{14}CO_2$ from the base-trap on day 30 which suggests that the major photodegradation pathway of DPX-Y6202 was by loss of CO_2. The next major pathway was by breakdown of the ester group to produce "DPX-acid."

Table 2. Soil Thin Layer Photodegradation of NC-302 (DPX-Y6202) at 365 nm on silty loam soil.

Irradiation (days)	% ^{14}C Applied												
	DPX-Y6202		DPX-ACID		Phenol-1		Unknown		Extractable			Unextractable	
	I	D	I	D	I	D	I	D	CO_2	I	D	I	D
0	97	95	--	--	--	--	1.7	2.3	--	99	97	2.9	2.6
3	67	97	5.3	--	0.5	--	4.9	2.9	0.6	78	100	16	0.7
7	61	87	12	--	0.6	--	6.0	3.8	2.1	80	91	9.6	1.5
14	60	89	2.5	0.6	0.3	0.8	6.6	7.9	6.6	69	98	21	2.3
30	47	91	4.7	0.2	1.4	0.3	18	9.8	17	73	102	12	2.0

I - Irradiated Sample

D - Dark Control

Conclusions

DPX-Y6202 undergoes soil photodecomposition at 365 nm with an estimated half-life of 30 days. Three major decomposition products were identified by comparison of R_f values of unknowns with reference compounds. Material balances were provided for this reaction which included both polar and non-polar unknowns. The concentration of unidentified metabolites increased steadily to a high of 18% of applied ^{14}C by day 30. The major photodecomposition pathway involved the elimination of CO_2 from DPX-Y6202.

Methods used for quantifying radiochemicals on TLC plates or $^{14}CO_2$ in base-traps was not given. The soils used in this study was poorly characterized Japanese soil and no comparisons with american soils were made. No attempt was made to identify large amount of unknown metabolites present on TLC.

STUDY 3

Cadwgan, G.E., McFetridge, R.D. 1985. Aerobic Soil Metabolism of [Phenyl-^{14}C(U)] DPX-Y6202. E.I. du Pont de Nemours and Co., Inc. Agricultural Chemicals Div., Wilmington, Delaware. Report No. AMR-329-85. Acc. No. 073548. Ref. Vol. 20, Sec. D2 exhibit 46.

Procedure

Two sieved soils, Flanagan silt loam and Woodstown sandy loam (characteristics in Table 3) were air-dried and 50g subsamples treated at 0.1 and 1.0 ppm (65 µCi, 100 and 1000 g ai/ha) with phenyl-[^{14}C]-DPX-Y6202 (Lot #CP-667, 99.4% pure) in acetone. After mixing and acetone evaporation, the soils were adjusted to 70% of moisture content holding capacity. Sodium hydroxide (10 ml, 0.1N) was placed in the sidearm of each flask to trap evolved CO_2. Treated flasks were incubated in the dark at 25°C and sampled after 0, 2, 5, 9, 16, 24, and 53 weeks. Base-traps were sampled every two weeks, fresh base added and the flasks purged (O_2) to maintain aerobicity.

One set of sterilized soil preparations were treated and stored as above to determine non-bacterial decomposition of DPX-Y6202. Large scale (250g) soil preparations were also treated and stored as above to allow for recovery and identification of metabolites.

Methodology

^{14}C in the base traps was quantified by LSC. $^{14}CO_2$ was precipitated as $Ba^{14}CO_3$ by the addition of saturated $Ba(OH)_2$ and the mixture centrifuged. The supernatant was radioassayed (LSC) to confirm the absence of other ^{14}C volatiles.

Soil samples were extracted four times by blending with 1:1 acetone:methylene chloride (v/v), centrifuging and decanting. Aged soil samples had to be extracted with polar solvents:1% H_3PO_4 (85%) in acetonitrile or methylene chloride:methanol:2M $(NH_4)_2CO_3$ 3:4:1 (v/v/v). Extracted soils were air dried for 2-3 days then combusted (O_2) and $14CO_2$ radioassayed (LSC).

Acetone/methylene chloride extracts were combined and evaporated to dryness (roto-evaporator, 45°C). The residue was redissolved in 1:1 methylene chloride/acetone (v/v), the solution concentrated (N_2, 45°C) then radioassayed (LSC) and analyzed by TLC.

Polar extracts were concentrated (roto-evaporater, 45°C), deionized water (50 ml) added, and then concentrated again to an aqueous phase. The aqueous solution was adjusted to pH 1.5 with H_3PO_4 (85%) and partitioned three times with ethyl acetate. Ethyl acetate extracts were combined, evaporated to dryness (roto-evaporator, 45°C) and the residue radioassayed (LSC) and analyzed by TLC.

TLC was conducted on silica gel plates developed to 15 cm in toluene:acetone: methanol:acetic acid, 150:60:12:1 (v/v/v/v). Radioactive areas were located by autoradiography and quantified by radioassay (LSC) of zonal scrapings or by use of a TLC-linear analyzer. Eluted unlabeled reference compounds were located by UV-fluorescence quenching and R_f values established for comparison with labeled metabolites.

Radioactive metabolites were separated by HPLC and identified by mass spectral analysis.

Results

Characteristics of the Woodstown sandy loam and Flanagan silt loam soils are shown in Table 3. Evolution of $^{14}CO_2$ from these ^{14}C-cellulose-treated soils demonstrated the presence of bacteria.

$^{14}CO_2$ was evolved from the non-sterile soils by week 2. Approximately 40% of the radioactivity applied to Flanagan soil was converted to $^{14}CO_2$ by week 53 whereas the conversion was 30% on Woodstown soil (Table 4). Less than 2% of radioactivity applied to the sterile soils evolved as $^{14}CO_2$ after 53 weeks (Table 6).

Before week 2 in the non-sterile soils, DPX-Y6202 was metabolized to polar intermediates which became progressively more tightly bound to soil. By week 53 the unextractable residue fraction averaged 24% for both non-sterile soils versus 5% for the sterile soils.

DPX-Y6202 was rapidly metabolized in non-sterile soils with an apparent half-life of less than one week to "DPX-Acid." The "DPX-acid" produced was further metabolized with an estimated half-life of 4 weeks on Flanagan soil and 8 weeks on Woodstown soil (Figure 2-3) based on % of applied ^{14}C.

The major metabolite of DPX-acid was phenol 4 which was present in both nonsterile soils by week 2. In Flanagan soil treated at 0.1 ppm, Phenol-4 levels were 26% of applied ^{14}C by week 2, decreased to 10% by week 9 and to 3% by week 53. At 1.0 ppm, phenol-4 levels were 30% by week 5, decreased to 20% by week 16, and to 5% by week 53 (Tables 4-5). In Woodstown soil at 0.1 and 1.0 ppm Phenol-4 reached a level of 11% by week 2 and 16 respectively which decreased to less than 2% by week 53 (Tables 4-5).

Phenols-1 and 3 were present in both non-sterile soils between weeks 2 and 5 but remained at levels below 7% through week 53. Two unidentified metabolites were present in most samples but remained at levels below 10% through week 53. One of these unknowns was unique to this phenyl-labeled study but the other was also present in a quinoxaline-labeled aerobic soil metabolism study (2).

DPX-Y6202 metabolized more slowly in sterile soils with an estimated half-life of 16 weeks on Flanagan soil and 24 weeks on Woodstown soil (Table 6, Figure 2-3).

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Table 3. Composition and Properties of soils used for Aerobic Soil Metabolism of phenyl-[^{14}C]-DPX-Y6202.

Soil	Sand	Silt	% Clay	OM[a]	CEC[b] meq/100 g	pH	% N
Woodstown Sandy Loam	61	32	7	1.4	5.2	6.4	0.05
Flanagan Silt Loam	3	80	17	4.4	21	6.1	0.39

[a] Organic matter.

[b] Cation exchange capacity.

Table 4. Distribution of ^{14}C residues following the aerobic aging of phenyl-[^{14}C]-DPX-Y6202 in loam soils at 0.1 ppm

Incubation	% ^{14}C applied											
	Woodstown											
(weeks)	DPX-Y6202	DPX-Acid	Phenol-1	Phenol-3	Phenol-4	a	b	c	d	e	CO_2	Total
0	108	--	--	--	--	--	--	--	--	0.3	--	108
2	13	67	0.8	*	11	--	--	4.1	0.3	8.3	0.1	104
5	14	47	--	--	8.5	6.9	--	4.2	2.2	15	0.3	99
9	10	38	2.8	*	9.4	0.9	0.3	4.5	2.2	27	1.5	96
16	9.6	10	4.7	*	7.9	3.3	0.3	1.0	0.5	21	18	86
24	9.8	16	3.0	0.7	3.0	3.4	1.7	1.1	0.0	17	24	87
53	11	11	0.3	0.8	1.1	4.6	3.0	1.5	1.1	30	33	97
	Flanagan											
0	104	--	--	--	--	--	--	--	0.6	1.1	--	106
2	4.4	55	--	--	26	5.3	--	2.5	0.5	5.0	0.1	99
5	2.7	25	2.0	*	21	2.0	9.6	2.8	3.8	18	4.4	90
9	6.1	14	2.1	*	9.5	5.9	3.0	3.5	3.9	26	14	87
24	5.2	7.5	2.5	1.9	8.2	3.3	3.8	0.5	--	22	25	80
53	4.1	9.3	0.2	1.7	2.7	4.2	1.1	2.7	0.4	21	38	86

a Unknown metabolite 1
b Unknown metabolite 2
c ^{14}C at the origin
d Other ^{14}C
e Non-extractable residues
* When phenols 1 and 3 could not be resolved the combined total was reported as phenol 1.

Table 5. Distribution of ^{14}C residues following the aerobic aging of phenyl-[^{14}C]-DPX-Y6202 in loam soils at 1.0 ppm

Incubation	% ^{14}C applied											
	Woodstown											
(weeks)	DPX-Y6202	DPX-Acid	Phenol-1	Phenol-3	Phenol-4	a	b	c	d	e	CO_2	Total
0	114	--	--	--	--	--	--	--	--	0.3	--	114
2	10	78	1.3	*	3.0	0.7	--	0.9	1.4	9.7	0.2	106
5	11	41	1.7	*	3.8	3.2	--	2.1	1.1	15	0.6	85
9	8.3	39	2.3	*	5.9	2.6	--	3.5	0.6	26	1.4	89
16	8.1	28	4.3	*	11	4.0	0.2	2.8	1.8	15	14	88
24	5.7	29	6.1	0.8	11	5.5	3.4	2.5	0.1	14	13	90
53	8.2	13	0.2	0.9	1.5	4.4	2.5	1.7	--	28	30	90
	Flanagan											
0	102	--	--	--	--	--	--	--	--	1.8	--	104
2	4.9	59	0.3	*	18	--	--	5.6	0.6	8.7	0.1	97
5	2.8	27	2.0	*	31	2.2	5.3	2.0	2.8	17	3.8	96
9	3.5	11	1.3	*	31	0.9	1.9	12	1.3	16	9.1	88
16	2.4	13	1.1	*	18	1.6	3.6	3.3	0.8	18	22	84
24	3.7	10	1.1	1.7	6.2	4.8	1.9	0.6	--	23	29	82
53	3.5	7.4	0.2	2.0	5.2	4.3	1.8	2.7	0.3	19	41	87

a Unknown metabolite 1
b Unknown metabolite 2
c ^{14}C at the origin
d Other ^{14}C

e Non-extractable residues
* When phenols 1 and 3 could not be resolved the combined total was reported as phenol 1.

Table 6. Distribution of ^{14}C residues following the aerobic aging of phenyl-[^{14}C]-DPX-Y6202 in sterile loam soils at 1.0 ppm.

Incubation	% ^{14}C applied											
	Woodstown											
(weeks)	DPX-Y6202	DPX-Acid	Phenol-1	Phenol-3	Phenol-4	a	b	c	d	e	CO_2	Total
0	114	--	--	--	--	--	--	--	--	0.3	--	114
2	93	0.2	--	--	--	0.4	--	0.3	2.9	1.8	0.2	99
5	87	11	--	--	1.1	0.2	--	0.2	0.2	1.3	0.2	101
9	95	1.8	0.3	*	0.1	--	--	1.1	--	2.1	0.7	101
16	64	24	4.2	*	--	--	--	1.2	3.3	10	0.6	101
24	52	24	5.9	--	0.8	--	--	1.1	1.4	0.3	1.2	87
53	29	57	0.3	0.6	1.3	1.2	0.1	0.4	3.1	8.1	0.5	101
	Flanagan											
0	102	--	--	--	--	--	--	--	--	1.8	--	104
2	93	0.6	--	--	--	--	--	0.4	0.1	2.3	0.1	96
5	87	2.0	0.2	*	--	--	--	0.5	--	2.9	0.3	93
9	86	5.1	1.4	*	0.3	1.1	--	2.3	0.1	2.5	0.3	99
16	51	10	--	--	--	--	--	0.6	1.3	4.7	1.5	70
24	20	59	1.3	--	3.9	--	--	0.6	2.7	2.5	0.7	91
53	78	14	0.5	4.9	1.1	0.8	0.7	0.1	0.4	2.6	1.9	105

a Unknown metabolite 1

b Unknown metabolite 2

c ^{14}C at the origin

d Other ^{14}C

e Non-extractable residues

* When phenols 1 and 3 could not be resolved the combined total was reported as phenol 1.

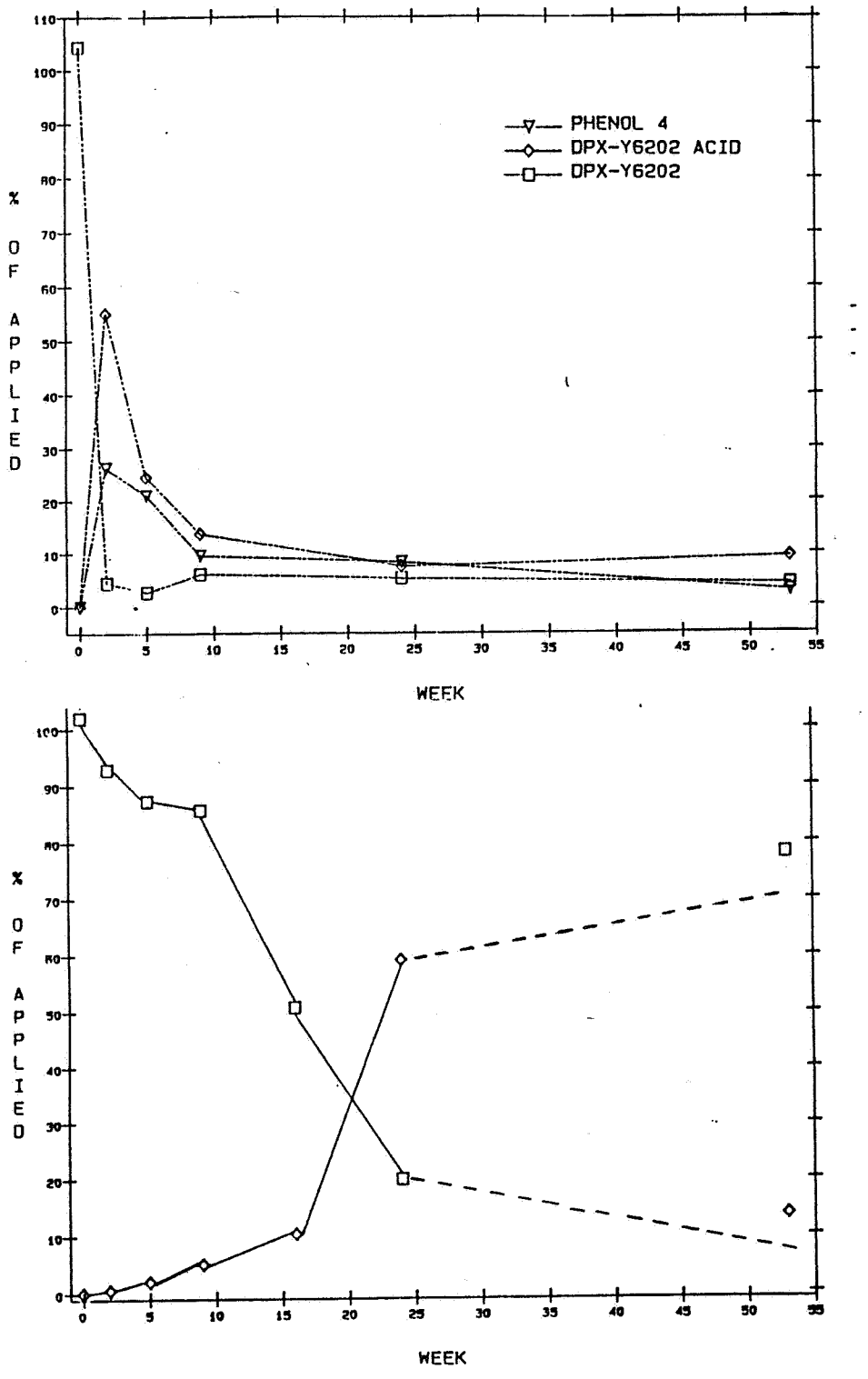

Figure 2. Aerobic metabolism of Phenyl-[^{14}C]-DPX-Y6202 in non-sterile (upper) and sterile (lower) Flanagan soil at 1.0 ppm.

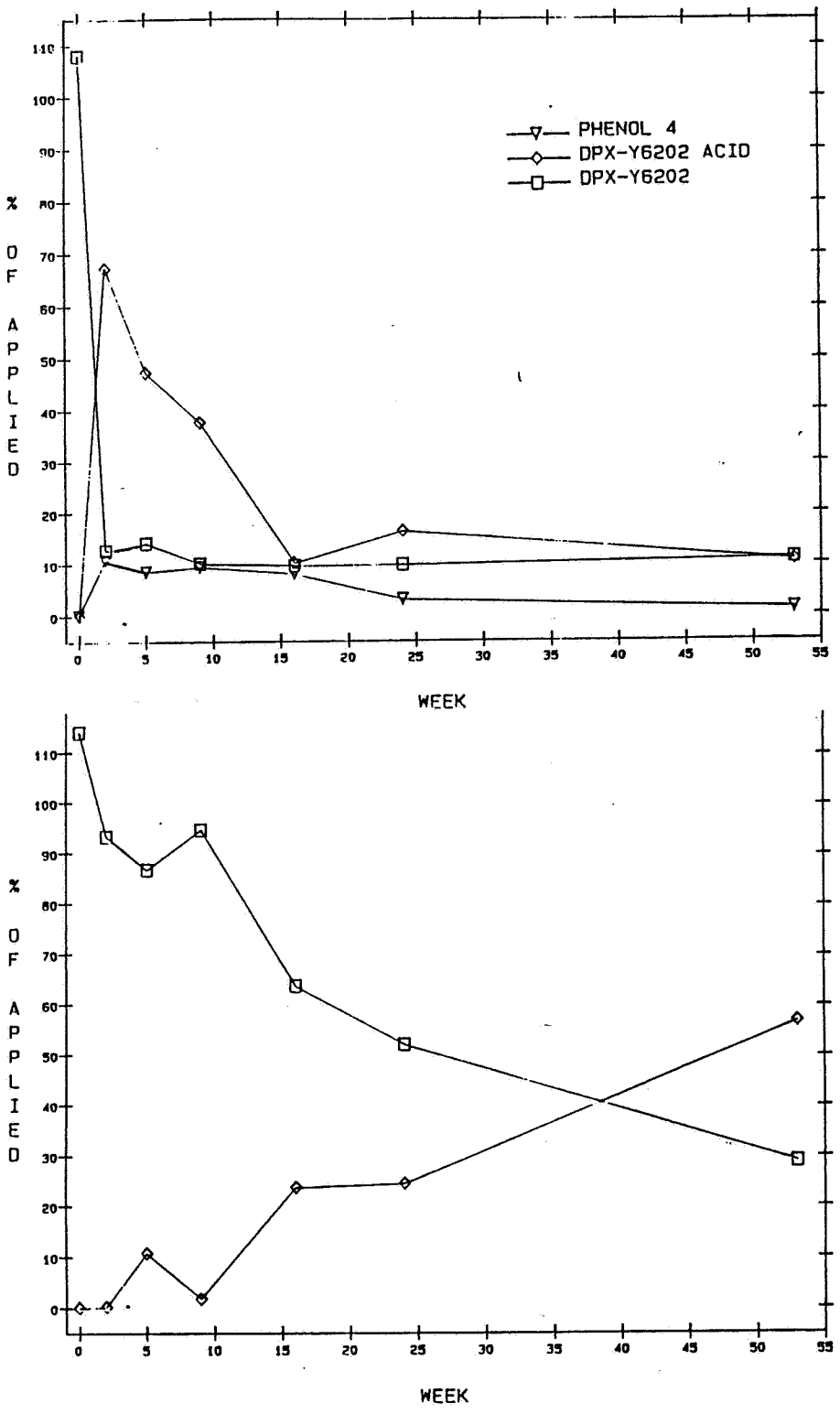

Figure 3. Aerobic metabolism of Phenyl-[^{14}C]-DPX-Y6202 in non-sterile (upper) and sterile (lower) Woodstown soil at 1.0 ppm.

Conclusion

DPX-Y6202 was rapidly metabolized in both Flanagan and Woodstown soils to "DPX-acid" which further degraded via cleavage of either ether group to produce phenols. Extensive mineralization of the phenyl ring of the above compounds to CO_2 occured after 10 or more weeks of aging.

Material balances provided ranged between 70-114%, and the description of all methods utilized in this study was made clear.

Residue decline curves were constructed which graphed the metabolism of DPX-Y6202 and its metabolites with time.

STUDY 4

Hirata, H., Wakabayashi T., Takano, S., Yamaguchi, I., T. Misato, February, 1985. Degradation of NC-302 in Soil. Nissan Chemical Industries, Ltd. Copyright by E.I. du Pont de Nemours and Co. Acc. No. 073548 Ref. Vol. 20, Sec. D2 exhibit 47.

Procedure

Two sieved soils (1 mm) Chiba silt loam and Nagano light clay (characteristics in Table 7) were oven-dried and incubated for one week in the dark. 25g subsamples were treated with phenyl-[^{14}C]-DPX-Y6202 (NC-302, 8.5 mCi/m mol, 99% pure) and quinoxaline-[^{14}C]-DPX-Y6202 (7.8 mCi m. mol, 98% pure) at 2.0 ppm. After mixing and solvent evaporation the soils were adjusted to 60% of moisture content holding capacity.

Aerobic Samples

Each flask was loosely fitted with aluminum foil.

Anaerobic Samples

Air in the flasks was displaced by N_2 gas and the flask tightly stoppered.

Sterile Samples

Chiba soil in each flask was autoclaved at 120°C for 20 min then treated with phenyl-[^{14}C]-DPX-Y6202. Each was tightly stoppered and stored in the dark (30°C).

Ethyl cellulose (40 ml) and potassium hydroxide (0.5N) were placed in the sidearm of each flask to trap CO_2 and organic volatiles. Soil and trap samples were collected between 0 and 360 days depending on the soil and aging conditions. Fresh solution was added to the traps at each sampling interval.

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Methodology

Soil samples were extracted twice by shaking with acetone, centrifuging, the supernatants pipetted, combined, and analyzed by TLC. Residual soil matter was then extracted twice by shaking with methanol:H_3PO_4 (1N) and filtered. Filtered soils were air-dried, combusted (O_2) and evolved $^{14}CO_2$ radioassayed (LSC).

The methanol/H_3PO_4 extracts were concentrated, deionized water (50 ml) added and the resulting aqueous solution extracted twice with ethyl acetate, the extracts combined and analyzed by TLC.

Subsamples of residual (extracted) soil was extracted seven times with methanol:2N phosphoric acid. It was assumed that each mixture was centrifuged, the supernate decanted or pipetted and combined. The supernatant was extracted with ethyl acetate (the number of times was not stated) and probably concentrated before analysis by TLC. Additional extractions of this soil were: 0.5N NaOH for 12 hr, twice with methanol, and then 0.5N NaOH for 30 min. The reviewer assumes that these extracts were then analyzed by TLC.

TLC analysis of the organic extracts was carried out using silica gel plates eluted with ether:hexane:acetic acid (10:10:0.3), benzene:ethyl acetate:acetic acid (4:2:1) or (16:8:1 v/v/v). Non-radioactive DPX-Y6202 and reference compounds were detected by UV quenching and radioactive materials by autoradiography.

It was assumed, not stated, that $^{14}CO_2$ in the traps were quantified by LSC. No confirmation method such as precipitation of $Ba^{14}CO_3$ was discussed. No method of quantifying TLC residues were discussed.

Results

Characteristics of the Chiba silty loam and Nagano clay soils are shown in Table 7. Decomposition products of DPX-Y6202 in these soils were similar to those found in studies 1-3 and depicted in Figure 1, Study 1.

Aerobic Metabolism

$^{14}CO_2$ was evolved from Chiba soil fortified with both radio-labeled compounds by day 7. Approximately 13% and 3% of applied phenyl-[^{14}C] and quinoxaline-[^{14}C] labels, respectively was converted to CO_2 by day 90 (Table 8). No organic volatiles were found in the base traps.

DPX-Y6202 was metabolized in both Chiba and Nagano soils from day 1 to polar intermediates which became progressively more tightly bound to the soil. Unextractable residues were 46 and 64% of applied phenyl and quinoxaline labels, respectively, by day 360 in Chiba soil and 44% on day 60 in Nagano soil for the phenyl label.

DPX-Y6202 was rapidly metabolized with an apparent half-life of less than one day to "DPX-Acid" in both soils. Generated "DPX-Acid" was further metabolized with the major metabolite being phenol-4. Phenol-4 was present from day 1 in phenyl-labeled Chiba soil, reached a peak of 6% by day 90 which decreased to 2% by day 360. In Nagano soil, phenol-4 peaked at 7% on day 60 when the experiment was terminated. Phenols-3 and 4 levels were not reported for the quinoxaline label in Chiba soil as expected.

Phenols-1 and 3 were present in both soils from day 1 but remained at levels below 5% throughout the experiment. Two unidentified metabolites were present in some samples but remained at levels below 7% throughout the experiment.

Anaerobic Metabolism

$^{14}CO_2$ was evolved from Chiba soil fortified with phenyl-labeled DPX-Y6202 by day 7 but not until day 30 with the quinoxaline-label. Evolved $^{14}CO_2$ peaked at 4.1% and 0.2% of applied phenyl-[^{14}C] and quinoxaline-[^{14}C], respectively by day 90 (Table 10). No organic volatiles were found in the base traps.

Anaerobic metabolism of DPX-Y6202 generated polar intermediates from day 1 which became progressively more tightly bound to Chiba soil. Unextractable residues were 50% of applied phenyl-[^{14}C] label, by day 90.

Phenyl-labeled DPX-Y6202 was rapidly metabolized with an apparent half-life of less than one day to "DPX-Acid". DPX-acid was further metabolized to phenol-4 which was present from day 1 and never exceeded 3% of applied ^{14}C.

Sterile Sample

No viability count was reported as proof of sterility. No CO_2 data was provided. Quantities of soil-bound polar intermediates were calculated by differences from applied ^{14}C and these were similar (41% on day 90) to that found with the non-sterile soils.

DPX-Y6202 appeared to be metabolized in sterile Chiba soil with a half-life of approximately 90 days (Table 11) compared to one day in non-sterile soils. Metabolic products were similar to those present in non-sterile soils, only at much lower levels. Peak concentration of DPX-acid was only 6% of applied ^{14}C and the levels of all other metabolites was less than 2% throughout the experiment.

Table 7. Composition and properties of soils used for aerobic and anaerobic metabolism of phenyl-[^{14}C]-DPX-Y6202.

Soil	Sand	Silt	% Clay	OM[a]	CEC[b] (meq/100g)	pH
Chiba silty loam	38	55	7.0	5.1	26	6.0
Nagano light clay	31	35	34	5.9	31	5.3

[a] Organic matter.

[b] Cation exchange capacity.

Table 8. Distribution of ^{14}C residues following the aerobic aging of phenyl-[^{14}C] and quinoxaline-[^{14}C]-DPX-Y6202 in silty loam soils at 2.0 ppm.

Incubation (weeks)	% ^{14}C applied											
	Phenyl-label											
	DPX-Y6202	DPX-Acid	Phenol-1	Phenol-3	Phenol-4	a	b	c	d	e	CO_2	Total
0	78	4.4	0.5	1.6	0.7	--	--	0.4	1.4	9.4	--	96
1	39	21	1.4	1.2	3.1	--	--	0.9	2.6	21	--	91
3	22	28	1.9	0.8	4.8	--	--	1.0	3.3	25	--	87
7	17	29	2.6	0.6	3.1	--	--	1.1	3.5	34	0.6	92
15	16	36	2.6	0.4	1.5	--	--	1.0	3.0	34	1.6	94
30	11	24	4.3	0.6	3.6	1.3	--	2.3	5.2	39	4.3	92
60	8.7	24	3.3	--	2.4	4.9	--	0.4	3.1	38	--	86
90	6.0	15	3.2	--	6.3	0.9	--	1.2	3.7	46	13	86
180	3.9	17	2.7	--	0.5	11	--	1.8	3.0	39		79
360	2.4	8.3	2.0	--	2.0	4.1	--	1.0	3.3	46		70
	Quinoxaline-label											
Incubation (weeks)												
7											0.2	
15											0.2	
30	9.3	23	1.3	--	--	1.6	5.0	3.3	6.7	47	1.1	98
60	8.3	22	4.1	--	--	4.3	2.6	2.3	5.3	46	--	96
90	5.6	15	3.2	--	--	4.0	4.9	1.1	3.0	50	2.6	89
180	4.1	16	3.0	--	--	11	3.0	1.1	6.4	48		93
360	2.8	9.3	2.0	--	--	5.5	6.4	0.7	5.9	64		98

a Unknown metabolite 1

b Unknown metabolite 2

c ^{14}C at the origin

d Other ^{14}C

e Non-extractable residues

Table 9. Distribution of ^{14}C residues following the aerobic aging of phenyl-[^{14}C]-DPX-Y6202 in light clay soil at 2.0 ppm.

	% ^{14}C applied										
Incubation (days)	DPX-Y6202	DPX-Acid	Phenol-1	Phenol-3	Phenol-4	a	b	c	d	e	Total
0	93	0.4	0.1	--	--	--	--	0.2	2.1	4.7	101
1	36	32	0.8	0.2	0.8	0.4	--	0.3	2.1	19	92
3	20	35	1.0	0.5	1.7	1.1	--	0.6	3.8	28	92
7	12	34	1.3	0.3	2.4	2.2	--	0.5	3.4	38	95
15	11	29	1.9	0.3	3.2	2.8	--	0.8	4.6	36	90
30	8.5	21	1.4	0.2	5.2	5.2	--	2.3	4.8	45	93
60	7.5	17	1.5	--	6.9	4.7	--	1.0	2.6	44	85

a Unknown metabolite 1

b Unknown metabolite 2

c ^{14}C at the origin

d Other ^{14}C

e Non-extractable residues

* Metabolites were separated by elution with solvent system A.

Table 10. Distribution of ^{14}C residues following the anaerobic aging of phenyl-[^{14}C]-DPX-Y6202 in silty loam soil at 2.0 ppm.

	% ^{14}C applied									
Incubation (days)	DPX-Y6202	DPX-Acid	Phenol-1	Phenol-3	Phenol-4	a	b	c	CO_2	Total
0	80	3.6	0.4	1.2	0.4	0.5	1.3	13	--	101
1	41	22	1.3	0.7	1.9	0.7	2.2	26	--	95
3	31	26	0.7	0.5	1.7	0.6	1.3	29	--	90
7	20	31	1.1	0.4	1.7	0.8	1.7	35	0.1	91
15	12	32	1.7	0.4	2.9	2.1	2.5	45	0.2	95
30	7.8	35	1.5	0.3	1.5	0.9	2.6	45	1.1	95
90	3.0	26	1.3	--	1.4	0.6	2.7	50	4.1	85

a ^{14}C at the 1 origin

b Other ^{14}C

c Non-extractable residues

Table 11. Distribution of ^{14}C residues following the aerobic aging of phenyl-[^{14}C]-DPX-Y6202 in sterilized silty loam soil at 2.0 ppm.

	% ^{14}C applied								
Incubation (days)	DPX-Y6202	DPX-Acid	Phenol-1	Phenol-3	Phenol-4	a	b	c	Total
1	95	0.6	0.2	1.3	0.1	0.2	1.0	1.2	99
3	80	0.9	0.1	0.8	0.2	0.2	1.1	16	84
7	75	1.3	0.2	1.0	0.2	0.2	1.0	21	79
15	73	2.2	--	0.5	--	0.1	0.8	23	77
30	62	3.4	0.3	0.9	0.4	0.3	0.7	32	68
90	49	6.3	0.5	1.1	0.7	0.4	1.2	41	59

a ^{14}C at the origin

b Other ^{14}C

c Non-extractable residues

Conclusion

DPX-Y6202 was rapidly metabolized (half-life ~1 day) in both chiba and Nagano soils when aged aerobically or when aged anaerobically (N_2) in Chiba soil to produce DPX-acid, soil-bound materials and several phenols by cleavage of the ether groups. Mineralization of the phenyl group to CO_2 occurred after 4 weeks of aerobic or anaerobic aging.

DPX-Y6202 was metabolized much slower in sterile Chiba soil (half-life ~90 days) by a pathway similar to that of the non-sterile soils.

Both soils used in this study were Japanese soils which were not compared to american soil.

Aerobic Metabolism

This study failed to meet guideline requirements since incubation temperatures was not provided, no attempts were made to ensure aerobicity of stored samples, no residue decline curves were provided, and the experimental procedures were poorly described.

Anaerobic Metabolism

This study failed to meet guideline requirements for the same reasons as above, in addition, the soils were not aged aerobically for 30 days prior to initiation of this study.

Sterile Samples

This study failed to meet guideline requirements because the data was limited, no proof of the maintainance of sterile conditions was offered, no CO_2 data was provided.

STUDY 5

Cadwgan, G.E., McFetridge, R.D. 1985. Anaerobic Aquatic Soil Metabolism of [Quinoxaline -[^{14}C]-DPX-Y6202 and [Phenyl - ^{14}C (u)]-DPX-Y6202. E.I. du Pont de Nemours and Co. Inc., Agricultural Chemicals Division, Wilmington, Delaware. Report No. AMR-350-85. Acc. No. 073548. Ref. Vol. 20, Sec. D2 exhibit 48.

Procedure

80g of wet Bradenton, FL and Landenburg, PA pond sediment (50g dry weight, characteristics in table 12) and 100 ml of pond water were added to centrifuge bottles. Several of these bottles were loosely capped and autoclaved (steam) on three consecutive days. Sediment in both autoclaved and non-autoclaved bottle sets were treated at 1.0 ppm (1000g ai/ha) with quinoxaline-[^{14}C]-(19.3 µCi/mg, 99% pure, Lot #CP-668) and phenyl [^{14}C]-DPX-Y6202 (65 µCi/mg, 99% pure, Lot #CP667). Bottles were flushed with nitrogen, capped and incubated in the dark at 25°C. These stored aquatic systems were harvested at intervals between 0 and 52 weeks.

Methodology

Samples were centrifuged, the supernatant decanted and a subsample radioassayed (LSC). The remaining solution was adjusted to pH 1.5 with H_3PO_4 (85%) and partitioned three times with ethyl acetate. Ethyl acetate extracts were combined, filtered, radioassayed (LSC) and evaporated to dryness (roto-evaporator, 45°C) the residue was taken up in acetone/methylene chloride, concentrated (N_2, 45°C) then radioassayed (LSC) and analyzed by TLC.

Sediment samples were extracted four times by blending with 1:1 acetone: methylene chloride (v/v), centrifuging and decanting. Extracts were combined, filtered and a subsample radioassayed (LSC). Remaining extract was evaporated to dryness (roto-evaporator, 45°C), the residue redissolved in 1:1 methylene chloride/acetone v/v), the solution concentrated (N_2, 45°C) then radioassayed (LSC) and analyzed by TLC.

Aged sediment samples had to be extracted with polar solvents:1% H_3PO_4 (85%) in acetonitrile or methylene chloride:methanol:2M $(NH_4)_2CO_3$ 3:4:1 (v/v/v). Extracted soils were air dried for 2-3 days, combusted (O_2) and $^{14}CO_2$ radioassayed (LSC).

Polar extracts were concentrated (roto-evaporator, 45°C), deionized water (50 ml) added, and then concentrated again to an aqueous phase. The aqueous solution was adjusted to pH 1.5 with H_3PO_4 (85%) and partitioned three times with ethyl acetate. Ethyl acetate extracts were combined, filtered and evaporated to dryness (roto-evaporator 45°C). The residue was taken up in 1:1 methylene chloride/acetone (v/v), the solution concentrated (N_2, 45°C) then radioassayed (LSC) and analyzed by TLC.

TLC was conducted on silica gel plates developed to 15 cm in toluene: acetone:methanol:acetic acid, 150:60:12:1 (v/v/v/v). Radioactive areas were located by autoradiography and quantified by radioassayed (LSC) of zonal scrapings or by use of a TLC-linear analyzer. Eluted, unlabeled reference compounds were located by uv-fluorescence quenching and R_f values established for comparison with labeled metabolites.

Results

Distribution of ^{14}C residues for quinoxaline-[^{14}C] and phenyl-[^{14}C]-DPX-Y6202 in FL and PA anaerobic systems (Tables 13-14) show that approximately 50% of applied ^{14}C was found in the pond sediment and 30% in pond water on day 0. This was due in part to the application rate exceeding the aqueous solubility of DPX-Y6202 (3).

For the non-sterile quinoxaline label the sediment extractable ^{14}C range was 50-70% and ^{14}C in the water phase decreased from approximately 30 to 2% by week 52. This probably resulted from the metabolism of DPX-Y6202 to less soluble metabolites which were adsorbed onto the sediment. The same was generally true for both sterile systems only at a slower rate.

With the phenyl-^{14}C studies low ^{14}C recoveries were obtained for week 14, 20, 32 and 52 samples (PA) and from one non-sterile FL sample (week 21). For these samples ^{14}C present in the water phase (2-21%) was less than normal (28-55%). This may have resulted from a loss of anaerobicity and evolution of $^{14}CO_2$. The sediment in these samples were comparable to those in samples with good recovery indicating that sediment anaerobic conditions were probably intact.

For phenyl-label samples with good recovery the range of sediment extractable ^{14}C (35-66%), sediment non-extractable (1-10%), and ^{14}C in the aqueous phase (28-55%) remained fairly constant through week 52. No significant migration of aqueous phenyl-^{14}C label into the sediment occurred. Total sediment ^{14}C was lower for the phenyl than the quionoxaline label (Fig. 4-5).

Bradenton FL Sediment

Anaerobic aquatic aging of quinoxaline-[^{14}C]-DPX-Y6202 in both non-sterile and sterile sediment resulted in rapid metabolism to "DPX-acid" with an estimated half-life of one day. Generated DPX-acid was further metabolized to phenols-1 and 2 by week 6 (Table 15, Fig. 4-5). Hydroxylation of phenol-2 to hydroxyphenol-2 (Figure 1, Study 1) occurred by week 13. Unknown metabolites 1 and 3 were also present from week 13, and polar material bound to the sediment was present from week 0. No phenol-4 was reported. There was little apparent differences between the sterile and non-sterile systems.

In both phenyl-labeled sterile and non-sterile systems DPX-Y6202 readily degraded to "DPX-acid" with an estimated half-life of one day. DPX-acid produced was converted to phenol-4 from week 2 and reached a peak of 76% of applied ^{14}C by week 52 (Table 17, Fig. 6-7) in the sterile sediment. Phenol-1 was also present as with the quinoxaline labeled system but phenol-2, and consequently hydroxyphenol-2 were not detected. Non-extractable residues were reported to decrease or change little with aging in both sterile and non-sterile phenyl labeled systems. Unknown metabolites 1 and 2 were present between weeks 6 and 13. Metabolite 3 was not reported as with the quinoxaline label.

Table 12. Composition and Properties of Sediments used for Anaerobic Aquatic Metabolism of quinoxaline-[^{14}C] and phenyl-[^{14}C]-DPX-Y6202.

Soil	Sand	Silt	%	Clay	OM[a]	CEC[b] meq/100g	pH[c]
Landenburg, PA Silt loam	36	58		6	6.8	21	6.7
Bradenton, FL Sand	91	9		0	6.3	12	7.4

[a] Organic matter.

[b] Cation exchange capacity.

[c] pH of pond water.

Table 13. Distribution of ^{14}C residues in Landenberg, PA and Bradenton, FL Anaerobic Aquatic Systems following the aging of quinoxaline-[^{14}C]-DPX-Y6202 at 1.0 ppm.

	% ^{14}C applied							
	BRADENTON, FL							
	Sediment				Sediment			
Incubation (weeks)	Organic extractable	Unextractable	Water	Total	Organic extractable	Unextractable	Water	Total
		Non-sterile				Sterile		
0	53	11	28	92	53	11	28	92
2	62	7	29	98	52	3	45	100
6	70	15	10	95	70	11	14	95
13	72	15	8	95	50	9	18	77
21	52	26	6	85	51	16	15	82
30	56	34	5	95	-	-	-	-
52	50	24	2	76	60	15	15	90
				LANDENBERG, PA				
0	38	3	65	106	38	3	65	106
2	65	5	30	100	41	2	52	95
6	77	5	16	98	53	4	44	101
14	60	3	11	74	49	3	30	82
20	74	16	4	94	55	5	28	88
32	54	32	2	88	-	-	-	-
52	57	20	2	79	63	11	27	101

Table 14. Distribution of ^{14}C residues in Landenberg, PA and Bradenton, FL Anaerobic Aquatic Systems following the aging of phenyl-[^{14}C]-DPX-Y6202 at 1.0 ppm.

	% ^{14}C applied							
	BRADENTON, FL							
	Sediment				Sediment			
Incubation (weeks)	Organic extractable	Unextractable	Water	Total	Organic extractable	Unextractable	Water	Total
	Non-sterile				Sterile			
0	59	10	28	98	59	10	28	98
2	38	1	48	89	36	1	55	91
6	42	3	41	86	38	1	48	86
13	47	4	43	94	49	2	48	98
21	29	18	14	61	44	3	48	95
30	38	6	50	94	-	-	-	-
52	35	2	47	83	42	1	52	95
	LANDENBERG, PA							
0	53	5	54	12	53	5	54	112
2	53	3	40	96	42	6	55	103
6	66	6	30	102	62	3	41	106
14	41	10	9	60	43	8	37	88
20	46	13	3	62	45	3	36	84
32	54	17	2	73	-	-	-	-
52	49	10	61	81	58	6	32	96

Table 15. Distribution of ^{14}C residues following the anaerobic aquatic aging of quinoxaline-[^{14}C]-DPX-Y6202 a 1.0 ppm in Bradenton, FL sediment.

Incubation (weeks)	% ^{14}C applied											
	non-sterile											
	DPX-Y6202	DPX-Acid	Phenol-1	Phenol-2	HP-2	Phenol-4	a	b	c	d	e	Total
0	58	20	-	-	-	-	-	-	1.9	2.2	11	92
2	4.4	64	-	-	-	-	-	-	9.3	13	7	98
6	5.2	43	5.9	13	-	-	-	-	5.6	7.3	15	95
13	1.4	15	4.5	4.0	8.9	-	8.9	8.9	29	-	15	96
21	2.0	11	7.0	2.9	9.9	-	2.9	9.3	13	-	26	84
30	2.5	15	9.3	4.3	15	-	8.1	-	8.7	-	34	97
52	1.3	9	9.5	3.9	20	-	3.6	-	5.5	-	24	76
	sterile											
0	58	20	-	-	-	-	-	-	1.9	22	11	92
2	15	61	-	-	-	-	-	-	14	7.1	3	100
6	5.5	35	8.5	17	-	-	-	-	9	8.7	11	95
13	1.7	18	3.2	5.3	7.8	-	6.2	4.5	28	-	9	82
21	3.3	13	4.6	3.9	5.2	-	11	5.2	17	3.9	16	83
52	1.9	19	9.0	8.1	3.3	-	12	7.6	12	1.4	15	90

[a] Unknown metabolite 1

[b] Unknown metabolite 3

[c] ^{14}C at the origin

[d] Other ^{14}C

[e] Non-extractable residues

HP-2 Hydroxyphenol-2

* When phenols 1 and 3 could not be resolved the combined total was reported as phenol 1.

Table 16. Distribution of ^{14}C residues following the anaerobic aquatic aging of quinoxaline-[^{14}C]-DPX-Y6202 at 1.0 ppm in Landenberg, PA sediment.

Incubation (weeks)	% ^{14}C applied											
	non-sterile											
	DPX-Y6202	DPX-Acid	Phenol-1	Phenol-2	HP-2	Phenol-4	a	b	c	d	e	Total
0	87	8.7	0.8	0.8	-	-	-	-	4.0	-	3.0	105
2	2.1	80	2.9	0.5	0.2	-	1.5	-	7.0	-	5.0	99
6	1.3	66	3.2	9.2	1.0	-	2.0	-	11	-	5.0	98
14	4.0	38	4.0	7.0	4.0	-	4.0	-	11	-	3.0	75
20	2.0	23	8.0	6.0	18	-	5.0	5.0	10	-	16	93
32	2.0	12	8.0	3.0	22	-	4.0	-	4.0	-	32	87
52	0.6	11	9.5	3.9	25	-	3.3	1.5	4.2	-	20	79
	sterile											
0	87	8.7	0.8	0.8	-	-	-	-	4.0	-	3.0	105
2	9.8	69	0.8	0.3	0.3	-	1.3	-	12	-	2.0	95
6	6.1	61	1.1	4.0	1.8	-	1.8	-	23	-	4.0	103
14	5.5	50	0.9	2.9	3.2	-	5.7	-	11	-	3.0	82
20	4.0	50	1.0	1.0	4.0	-	5.0	3.0	15	-	5.0	88
52	1.1	72	3.3	2.3	1.9	-	4.6	2.1	3.4	-	11	102

[a] Unknown metabolite 1

[b] Unknown metabolite 3

[c] ^{14}C at the origin

[d] Other ^{14}C

[e] Non-extractable residues

HP-2 Hydroxyphenol-2

* When phenols 1 and 3 could not be resolved the combined total was reported as phenol 1.

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Table 17. Distribution of ^{14}C residues following the anaerobic aquatic aging of phenyl-[^{14}C]-DPX-Y6202 at 1.0 ppm in Bradenton, FL sediment.

Incubation (weeks)	% ^{14}C applied											
	non-sterile											
	DPX-Y6202	DPX-Acid	Phenol-1	Phenol-2	HP-2	Phenol-4	a	b	c	d	e	Total
0	66	18	0.3	-	-	-	-	-	1.8	1.3	10	97
2	1.1	49	-	-	-	29	-	-	4.5	3.0	1.4	88
6	-	44	3.0	-	-	32	2.0	1.0	2.1	-	4.0	88
13	0.7	20	5.1	-	-	51	6.0	4.0	4.0	-	3.9	95
21	1.3	16	3.9	-	-	15	2.2	-	1.3	-	18	58
30	2.9	17	16	-	-	25	12	1.2	11	2.5	5.7	94
52	0.7	11	3.1	-	-	59	2.2	1.6	1.2	0.4	2.4	83
	sterile											
0	66	18	0.3	-	-	-	-	-	1.8	1.3	10	97
2	7	62	-	-	-	18	-	-	2.8	2.5	0.9	93
6	4.7	31	6.4	-	-	39	-	-	2.4	1.4	2.0	87
13	2.9	27	3.7	-	-	55	2.2	0.8	3.9	1.4	1.6	99
21	1.8	25	8.2	-	-	48	5.5	-	1.8	-	3.2	93
52	0.9	12	1.3	-	-	76	1.7	0.7	0.7	0.7	1.1	95

[a] Unknown metabolite 1

[b] Unknown metabolite 2

[c] ^{14}C at the origin

[d] Other ^{14}C

[e] Non-extractable residues

HP-2 Hydroxyphenol-2

* When phenols 1 and 3 could not be resolved the combined total was reported as phenol 1.

Table 18. Distribution of ^{14}C residues following the anaerobic aquatic aging of phenyl-[^{14}C]-DPX-Y6202 at 1.0 ppm in Landenberg, PA sediment.

Incubation (weeks)	% ^{14}C applied											
	non-sterile											
	DPX-Y6202	DPX-Acid	Phenol-1	Phenol-2	HP-2	Phenol-4	a	b	c	d	e	Total
0	91	10	-	-	-	-	-	-	3.7	2.0	4.8	112
2	2.1	76	1.7	-	-	8.5	-	-	3.6	1.3	3.4	97
6	5.0	63	8.9	-	-	12	0.6	-	4.2	2.2	5.8	102
13	2.7	28	7.1	-	-	4.2	3.2	1.0	3.6	0.4	11	61
20	2.9	22	8.8	-	-	11	3.4	3.4	1.5	0.0	13	65
32	3.3	28	11	-	-	7.1	3.2	0.5	2.0	1.3	17	73
52	1.1	24	10	-	-	22	4.7	2.5	2.7	0.9	12	81
	sterile											
0	91	10	-	-	-	-	-	-	3.7	2.0	4.8	112
2	13	70	0.2	-	-	8.9	-	-	3.4	1.5	6.3	103
6	13	57	4.2	-	-	22	-	-	5.2	1.6	2.8	106
14	5.1	48	0.5	-	-	15	4.7	-	4.3	3.4	7.7	89
20	3.2	45	1.6	-	-	22	3.2	-	2.4	-	3.3	80
52	1.4	51	3.1	-	-	24	4.6	0.8	1.8	1.3	7.5	95

[a] Unknown metabolite 1

[b] Unknown metabolite 2

[c] ^{14}C at the origin

[d] Other ^{14}C

[e] Non-extractable residues

HP-2 Hydroxyphenol-2

* When phenols 1 and 3 could not be resolved the combined total was reported as phenol 1.

Landenberg, PA Sediment

The same observation were made for both quinoxaline- and phenyl-[^{14}C]-DPX-Y6202 metabolism in this sediment as in the FL sediment above. These data are shown in Tables 16 and 18.

Conclusions

Both phenyl- and quinoxaline-[^{14}C]-DPX-Y6202 were rapidly degraded in anaerobic aquatic systems to "DPX-acid" which was further metabolized by cleavage of the ether groups to produce various phenols. There was little difference between sterile and non-sterile sediments but significant product differences occurred with the DPX-label used. The quinoxaline-label resulted in phenol-2, hydroxyphenol-2, and no phenol-4. The phenyl-label yielded no phenol-2 or hydroxyphenol-2 but large amounts of phenol-4. Recovery was poor for several phenyl-label samples and it was believed that anaerobic conditions may have been lost in the aqueous phase (resulting in evolved $^{14}CO_2$) while being maintained in the sediments.

Since the application rate exceeded the aqueous solubility of DPX-Y6202, more than 50% was present in the sediment on day 0. There was some migration of ^{14}C into the sediment from the aqueous phase with the quinoxaline-label but not with the phenyl-label.

Unknown metabolites 1 and 2 were both present at levels >0.01 ppm and should be identified.

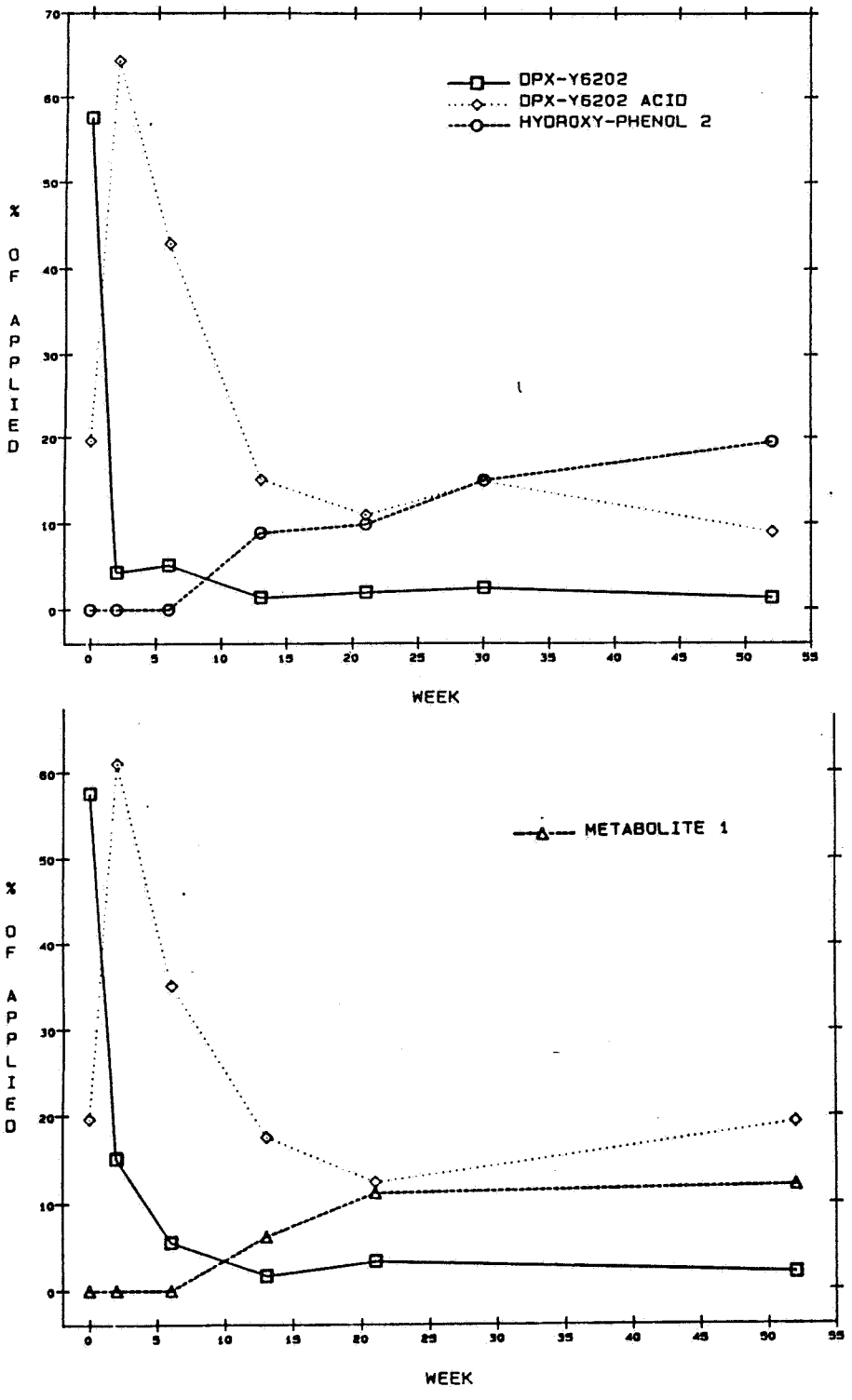

Figure 4. Distribution of ^{14}C residues following the anaerobic aquatic aging of quinoxaline [^{14}C]DPX-Y6202 in non-sterile (upper) and sterile (lower) Bradenton, FL sediment at 1.0 ppm.

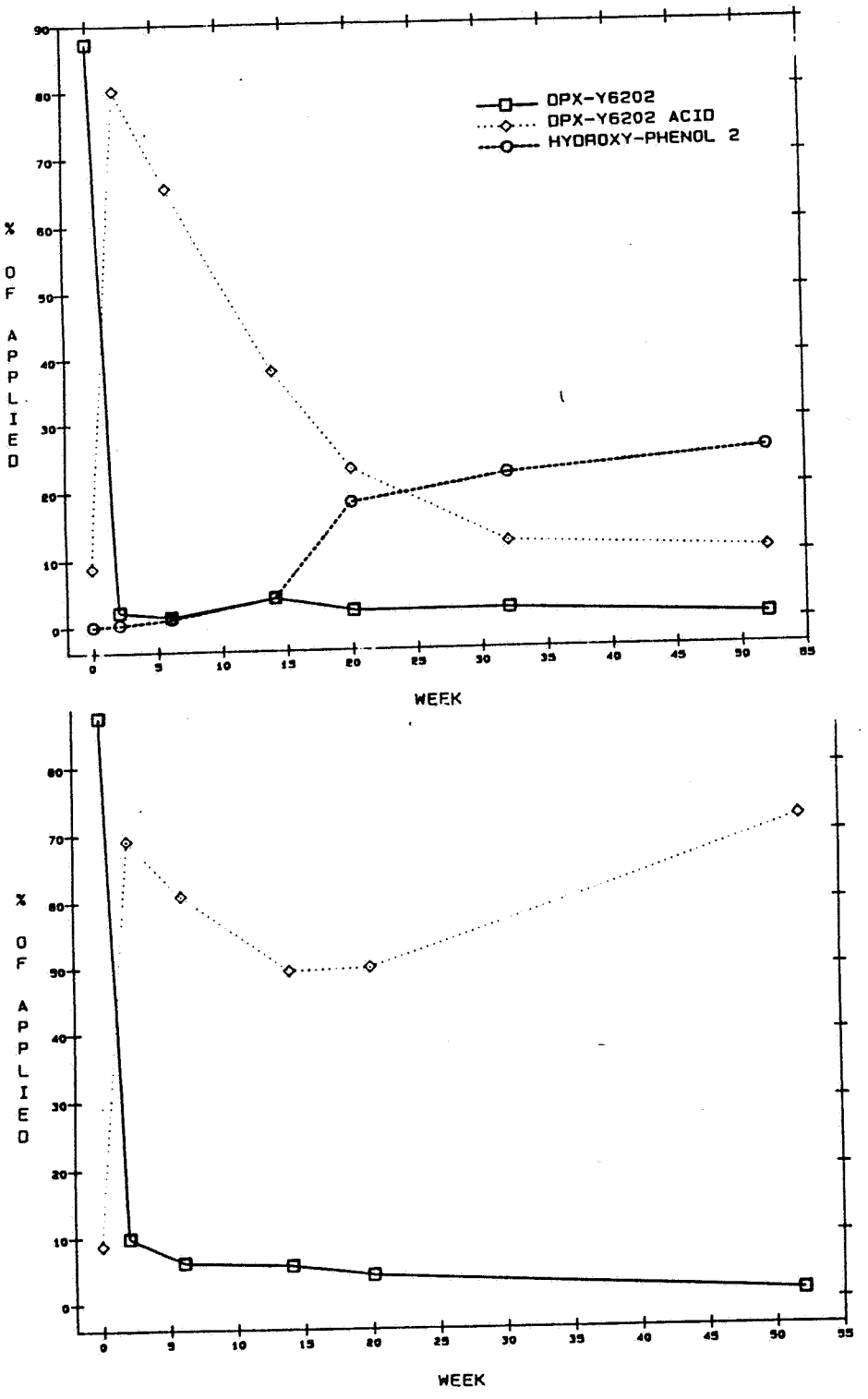

Figure 5. Distribution of ^{14}C residues following the anaerobic aquatic aging of quinoxaline [^{14}C]DPX-Y6202 in non-sterile (upper) and sterile (lower) Landenberg, PA sediment at 1.0 ppm.

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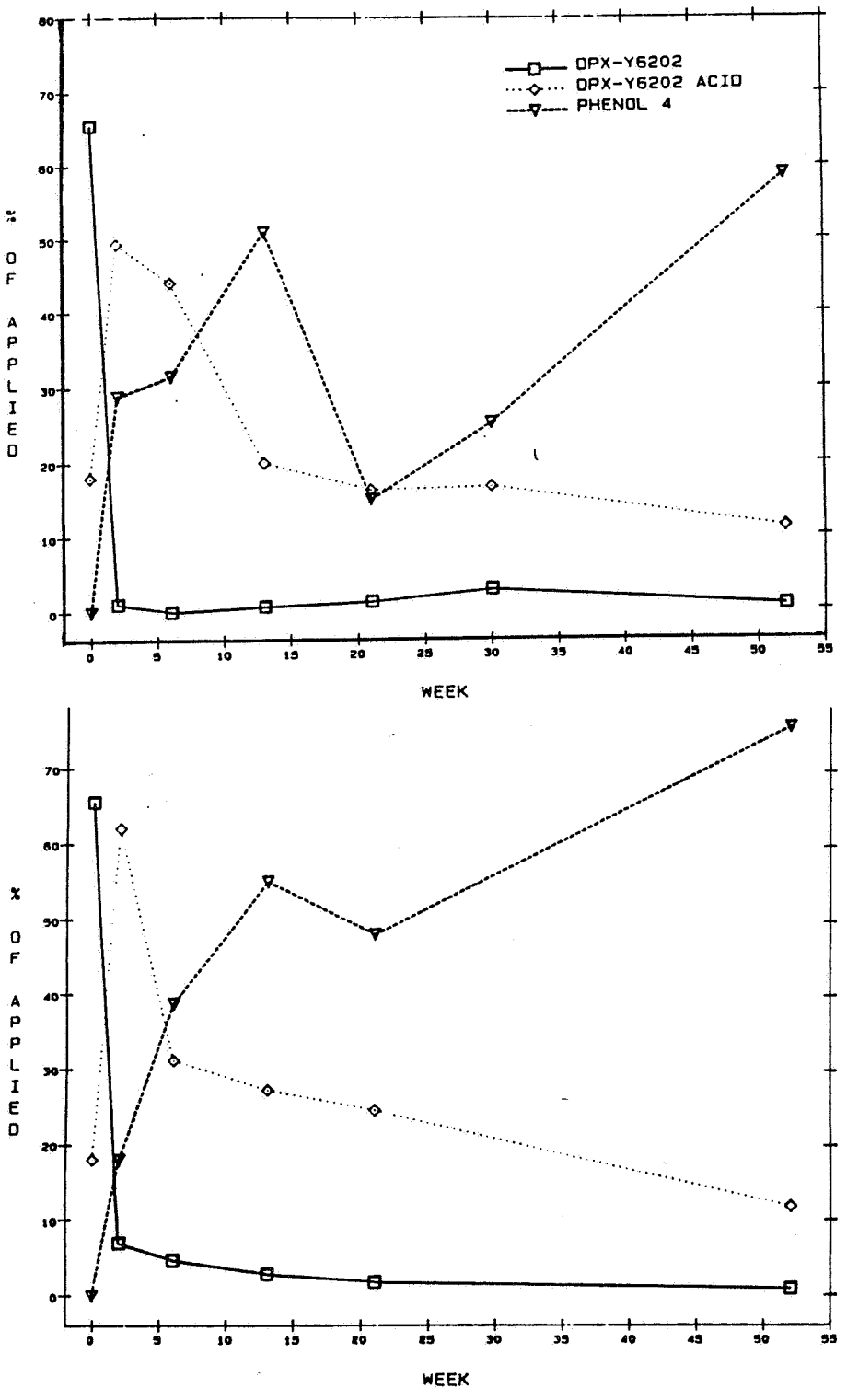

Figure 6. Distribution of ^{14}C residues following the anaerobic aquatic aging of phenyl-[^{14}C]-DPX-Y6202 in non-sterile (upper) and sterile (lower) Landenberg, PA sediment at 1.0 ppm.

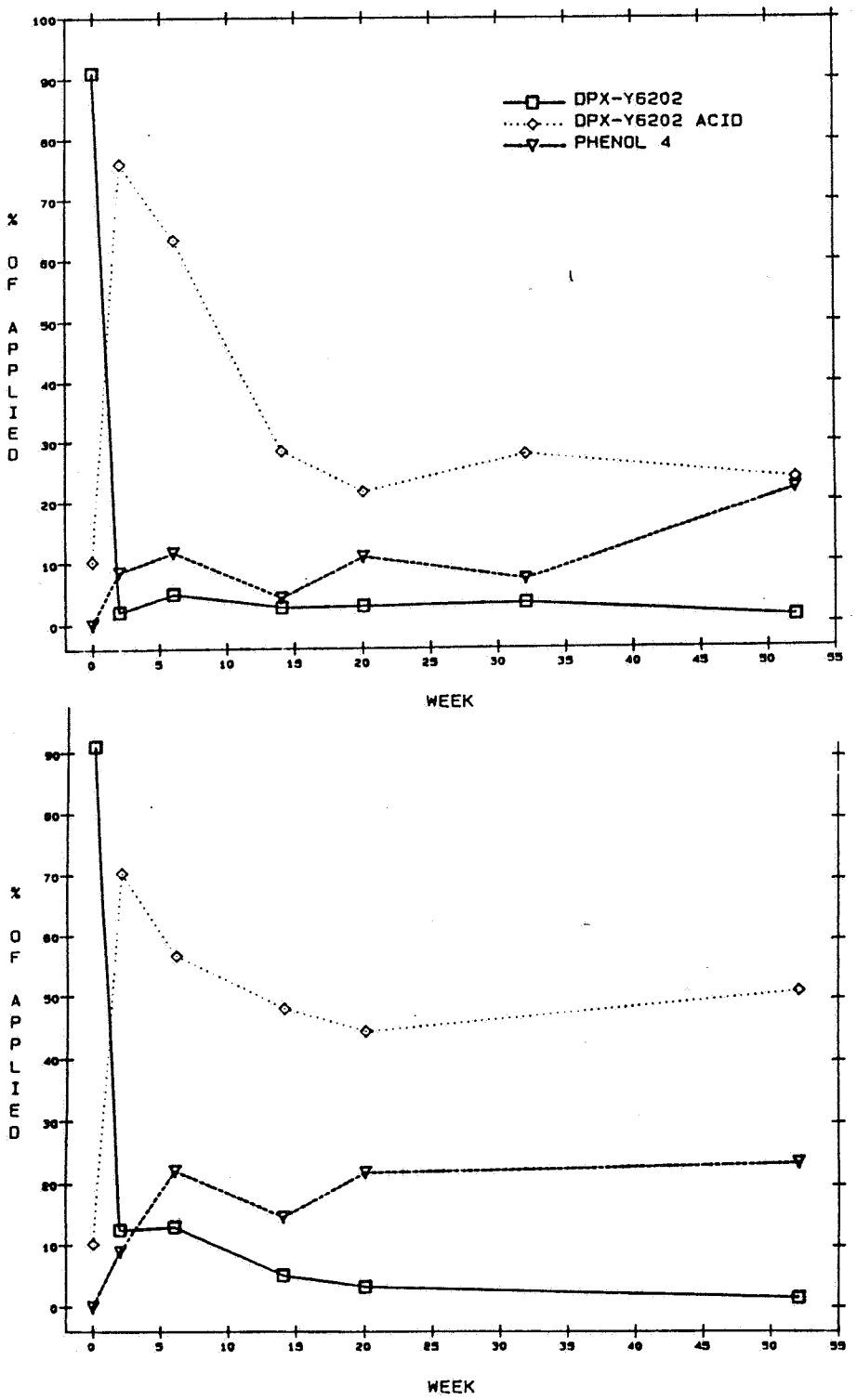

Figure 7. Distribution of ^{14}C residues following the anaerobic aquatic aging of quinoxaline-[^{14}C]-DPX-Y6202 in non-sterile (upper) and sterile (lower) Bradenton, FL sediment at 1.0 ppm.

Desorption: ^{14}C removed from the soil (C_{2a}) at equilibration was determined by subtracting ^{14}C in the aqueous phase at the start of the day from ^{14}C after 24 hr.- equilibration. ^{14}C remaining on the soil was equal to the difference between the C_{2a} value derived and C_s from the previous day.

Desorption data were plotted on log-log paper to generate the desorption isotherm. Desorption distribution coefficients (K_d) and $K_{d,OM}$), and slopes of the isotherms ($1/n_d$) were determined as in the adsorption study.

Theoretical desorption distribution coefficients (K_d') were calculated from the experimental adsorption distribution coefficient values using the Hornsby equation (5):

$$K_d' = K_a \, (n_a/n_d) \times S_m \, (1-n_a/n_d)$$

where S_m = maximum concentration of test compound on the soil

R_f values for each test compound was calculated by dividing the average distance traveled from the origin by 10 (CM).

Results

Adsorption: DPX-Y6202 was moderately adsorbed to the sandy loam soils (K_a = 4.8 and 5.6) (Table 21), but was very strongly adsorbed to the Flanagan (K = 13) and the Keyport (K_a = 14) soils of high (4-7%) organic content.

The slope of the Freundlich adsorption isotherm ($1/n_a$) was approximately 0.80 (~1.0) for all four soils. This indicated that adsorption was not affected significantly by DPX-Y6202 concentration. DPX-Y6202 adsorption was similar to that of diuron but approximately ten times greater than that of terbacil. Correlation coefficients for % organic matter versus K_a indicated a strong correlation for DPX-Y6202 (r = 0.92) and terbacil (0.97) and a poor correlation for diuron (r = 0.60).

Desorption: DPX-Y6202 was poorly desorbed from all four soils, diuron was slightly better and terbacil much more easily desorbed based on $1/n_d$ values. K_d values of DPX-Y6202 were not directly comparable with those of terbacil or diuron since the S_m values of DPX-Y6202 were much lower than those used for terbacil (8x) and diuron (16x),(Figure 9).

K_d values calculated from experimental K_a values, were in excellent agreement with experimental K_d values.

Correlation coefficient (r) for percent organic matter versus $1/n_d$ were -0.88, +0.99 and -0.83 for DPX-Y6202, terbacil and diuron respectively. This indicated a strong negative correlation for DPX-Y6202 and diuron and a strong positive correlation for terbacil.

Soil TLC: The mobility of DPX-Y6202, as measured by R_f values appeared to be independent of percent organic matter for all four soils (Figure 10). R_f values (Table 20) characterized DPX-Y6202 as a Class 1 (immobile) compound on all soils tested which was similar to diuron and different from the mobile terbacil.

Table 19. Composition and Properties of Soils used for Adsorption/Desorption Study of DPX-Y6202

Soil	Sand	Silt	Clay	OM[a]	CEC[b]	pH
	%				meq/100g	
Woodstown	60	33	7	1.1	5.3	6.6
Cecil	61	21	18	2.1	6.6	6.5
Flanagan	2	81	17	4.3	21	5.4
Keyport	12	83	5	7.5	16	5.2

[a] organic Matter.
[b] Cation Exchange Capacity.

Table 20. Soil Thin-Layer Chromatography of DPX-Y6202, Terbacil and Diuron

Soil-Type	R_f Value		
	DPX-Y6202	Terbacil	Diuron
Woodstown Sandy Loam	0.03	0.64	0.21
Cecil Sandy Loam	0.02	0.44	0.10
Flanagan Silt Loam	0.03	0.36	0.08
Keyport Silt Loam	0.05	0.28	0.05

Table 21. Adsorption/Desorption Parameters of DPX-Y6202, Terbacil, and Diuron on Four Soils*

Soil Type	K^1 (µg/g)			K^2 (µg/g)			$1/n^3$		
	DPX-Y6202	Terbacil	Diuron	DPX-Y6202	Terbacil	Diuron	DPX-Y6202	Terbacil	Diuron
Adsorption (a)									
Woodstown Sandy Loam	4.8	0.38	4.0	436	35	364	0.98	0.95	0.79
Cecil Sandy Loam	5.6	0.96	8.8	267	46	419	0.92	0.85	0.80
Flanagan Silt Loam	13	1.3	18	302	30	419	0.82	0.88	0.82
Keyport Silt Loam	14	2.0	12	187	25	160	0.86	0.92	0.79
Desorption (d)									
Woodstown Sandy Loam	0.71 **(0.77)	0.71 (0.76)	4.1 (4.2)	65	65	370	0.32	0.51	0.56
Cecil Sandy Loam	0.55 **(0.55)	1.2 **(1.4)	6.1 **(6.5)	26	57	290	0.17	0.54	0.31
Flanagan Silt Loam	0.47 **(0.47)	1.9 **(1.8)	6.5 **(6.8)	11	44	150	0.06	0.58	0.11
Keyport Silt Loam	0.41 **(0.41)	2.4 **(2.4)	6.6 **(6.4)	5	32	88	0.03	0.63	0.12

* Experimental data for terbacil and diuron are taken from Reference 5.
**Calculated from experimental Ka using the Hornsby equation

[1]Freundlich adsorption/desorption distribution coefficient.
[2]Coefficient of adsorption per unit organic matter.
[3]Slope of the Freundlich adsorption isotherm.

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CONCLUSIONS

Information on the sorption and mobility of parent DPX-Y6202 only was provided. Adsorption of DPX-Y6202 was similar to that of diuron in all four soils tested and there was a good correlation between K_a and soil organic matter. The slope of the Freundlich adsorption isotherm indicated that adsorption was independent of DPX-Y6202 concentration.

DPX-Y6202 was poorly desorbed from all four soils. Calculated K_a values were similar to experimental values. There was a negative correlation between % organic matter and $1/n_d$ for DPX-Y6202.

R_f values characterized DPX-Y6202 as a Class 1, immobile compound on all four soils.

Soils used in this study were not aged for 30 days as required to allow for characterization of the mobility of DPX-Y6202 degradates.

STUDY 7

Wakabayashi, T., Hirata, H. and Takano, S. February 1985. Mobility of NC-302 in soil. Nissan Chemical Industries, Ltd. Copyright E. I. du Pont de Nemours & Co. Acc. No. 073548. Ref. Vol. 20, Sec. D2, exhibit 50.

Procedure

Four soils, Aichi, Gunma, Chiba and Nagano were air-dried and sieved (0.25 mm). Characteristics of these soils are shown in Table 22. Distilled water was added to sieved soils (1:1v/g) and the resulting slurry applied to chromatography plates. Soil plates were air-dried for 3 days then treated with [^{14}C]-NC-302 (phenyl-[^{14}C]-DPX-Y6202) and radiolabeled NC-302 acid, 2,4-D and DDT (Table 23) at 0.1-1.0 µg/cm^2 in triplicate.

Methodology

Each soil TLC plate was eluted to 10 cm. with distilled water, air-dried overnight, and developed by autoradiography. Radioactive areas were also detected by TLC radioscanograms. Rf values were calculated by dividing the distance from origin to peak maximum (cm) by the developing distance (cm).

Values of soil/water relationships (Kd) were calculated from the Rf values on soil TLC using the following equation:

$$Rf = \frac{1}{1 + Koc. \frac{\%\ OM.}{100}\ ds\ \left(\frac{1}{\frac{\theta^2}{3}} - 1\right)}$$

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where θ is the soil pore fraction, ds is the density of soil, om is organic matter and Kom is the organic matter adsorption coefficient.

Results

The movement of each chemical on the four different soil TLC plates are summarized in Table 24. NC-302 and DDT remained at the origin on each plate. NC-302 acid and 2,4-D migrated with 2,4-D being more mobile than NC-302 acid.

Using the Helling-Turner pesticide mobility classification for Hagerstown soil (6) for these studies on Japanese soils, NC-302 and DDT were classified as Class 1 (immobile), 2,4-D and NC-302 acid were classified as low mobility.

Kd values calculated from experiemntal R_f values are shown in Table 25. Kd values for NC-302 and DDT could not be obtained since $R_f = 0$. Kd values for NC-302 ranged from 2-13, all low values which are consistent with a pesticide of low mobility.

Table 22. Composition and Properties of Soil Used for Soil TLC of Phenyl-[^{14}C]-DPX-Y6202.

Soil	Sand	Silt %	Clay	OM[a]	CEC[b] (m.e./100g)	pH	ds
Aichi sandy clay loam	59	19	23	0.5	7.0	6.4	2.7
Gunma sand	86	11	3.5	2.0	10	5.3	2.7
Chiba silty loam	38	55	7.0	5.1	26	6.0	2.6
Nagano light clay	31	35	34	5.9	31	5.3	2.6

[a] Organic Matter
[b] Cation Exchange Capacity
[c] density of solid soil

Table 23. Radiochemical Purity of [^{14}C]-NC-302 and Reference Materials

Common Name	Chemical Name	Specific activity (mCi/mmol)	Radiochemical purity (%)
^{14}C-NC-302	ethy]-2-[4-(6-chloro-2-quinoxalinyloxy) [U-^{14}C]-phenoxy]-propionate	8.5	99
^{14}C-NC-302 acid	2-[4-(6-chloro-2-quinoxalinyloxy)[U^{14}C]-phenoxy]-propionic acid	8.5	97
^{14}C-2,4-D	2m4-dichlorophenoxy-[2-^{14}C]-acetic acid	55.0	99
^{14}C-DDT	dichlorodi-[U-^{14}C]-phenyltrichloro ethane	85.0	98

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Table 24. Rf Values of NC-302, NC-302 Acid, 2,4-D and DDT from Soil TLC

Soil	NC-302	NC-302 acid	2,4-D	DDT
Aichi	0.00	0.21	0.49	0.00
Gunma	0.00	0.24	0.34	0.00
Chiba	0.00	0.15	0.23	0.00
Nagano	0.00	0.10	0.15	0.00

Table 25. Kd Values of NC-302 Acid and 2,4-D Calculated from Soil TLC R_f Values

Soil		NC-302 acid			2,4-D		
	O	R_f	KOM	Kd	R_f	KOM	Kd
Aichi	0.5	0.21	396	2.0	0.49	110	0.6
Gunma	0.6	0.24	145	2.9	0.34	89	1.8
Chiba	0.7	0.15	159	8.1	0.23	94	4.8
Nagano	0.7	0.10	218	13	0.15	137	8.1

Conclusions

The mobility of NC-302 (DPX-Y6202) and its major metabolite NC-302 acid was determined by soil TLC in four soils. NC-302 was found to be immobile and NC-302 acid of low mobility in four Japanese soils.

The properties of these soils were not compared to those of American soils. Soils were not aged aerobically for 30 days with NC-302 to allow for the formation of degradates other than NC-302 acid.

STUDY 8

Wakabayashi, T., Hirata, H. and Takano, S. February 1985. Soil adsorption and desorption of NC-302 in soil. Nissan Chemical Industries, Ltd. Copyright E. I. du Pont de Nemours & Co. Acc. No. 073548. Ref. Vol. 20, Sec. D2, exhibit 51.

Procedure

Four soils, Aichi, Gunma, Chiba and Nagano were air-dried and sieved (1 mm). Characteristics of these soils are shown in Table 22 (Study 2). Soil samples were oven-dried then treated with [^{14}C]-NC-302(phenyl-[^{14}C]-DPX-Y6202) and radiolabeled NC-302 acid, 2,4-D and DDT (Table 23, Study 7) at four levels between 0.02 and 0.20 µg/ml.

Adsorption: Soil equilibrium-times at 23°C were established as 3 hr for NC-302, DDT, and 2,4-D and 24 hr for NC-302 acid. 20 ml of radiochemical solution was shaken with 2g of soil for either 3, or 24 hr, centrifuged, the supernatant decanted and radioassayed (LSC) in duplicate.

Desorption: At the end of each equilibrium period, 13 ml of the supernatant was removed and 15 ml of distilled water added to each tube. The tube was shaken and centrifuged as in the adsorption experiment and the radioactivity of the supernatant measured (LSC) in duplicate.

Methodology

Adsorption: Freundlich coefficients (k) were obtained by plotting Log S (µg/g) versus Log C (µg/ml), which resulted in a linear curve of slope 1/N and intercept K. 1/N indicates the degree of non-linearity of adsorption isotherms. The soil concentration of the chemical, S'(µg/g) was calculated as follows:

$$S = \frac{V}{m} (A - C)$$

where A = initial concentration of the chemical solution (µg/ml)
C = equilibrium concentration of the chemical solution (µg/ml)
V = initial volume of the chemical solution (20 ml)
m = soil mass (2g).

Concentration of each chemical in solution was determined using the following equation:

$$\text{Concentration (µg/ml)} = \frac{\text{dpm/ml}}{\text{Specific activity of chemical (dpm/µg)}}$$

The adsorption coefficient (Ka) was described as a function of soil organic matter content (K_{OM}) by multiplying Ka by 100/% OM)

Desorption: The concentration of each chemical in soil after desorption, S'(µg/g) was calculated using the following equation:

$$S' = \frac{1}{m} (V \cdot A - V' \cdot C - V \cdot C')$$

where A = initial concentration of the chemical solution (µg/ml)
C = concentration of the chemical solution after adsorption (µg/ml)
C' = concentration of the chemical solution after desorption (µg/ml)
V = volume of chemical solution initially added (20 ml)
V' = volume of chemical solution removed after adsorption (15 ml)
m = soil weight (2.0g)

Desoprtion parameters, K', 1/N' and K'oc, were derived by regression analysis of data obtained for C' and S' as described for adsorption.

Results

Figure 8 shows the equilibrium adsorption isotherms for NC-302. The adsorption/desorption parameters for NC-302, NC-302 acid, 2,4-D and DDT (Tables 26 and 27) demonstrate that DDT was immobile, and 2,4-D mobile in the four Japanese soils tested. Mean Ko_M values for each chemical in the

four soils were; NC-302:1816, NC-302 acid:476, DDT:42606 and 2,4-D:119. Comparing these values, the order of adsorptivity was:DDT > NC-302 > NC-302 acid > 2,4-D. Mean K'_{OM} values of each chemical in four soils were; NC-302:16769, NC-302 acid:674, DDT:49964 and 2,4-D:135. The order of desorptivity was as follows:2,4-D > NC-302 acid > NC-302 > DDT.

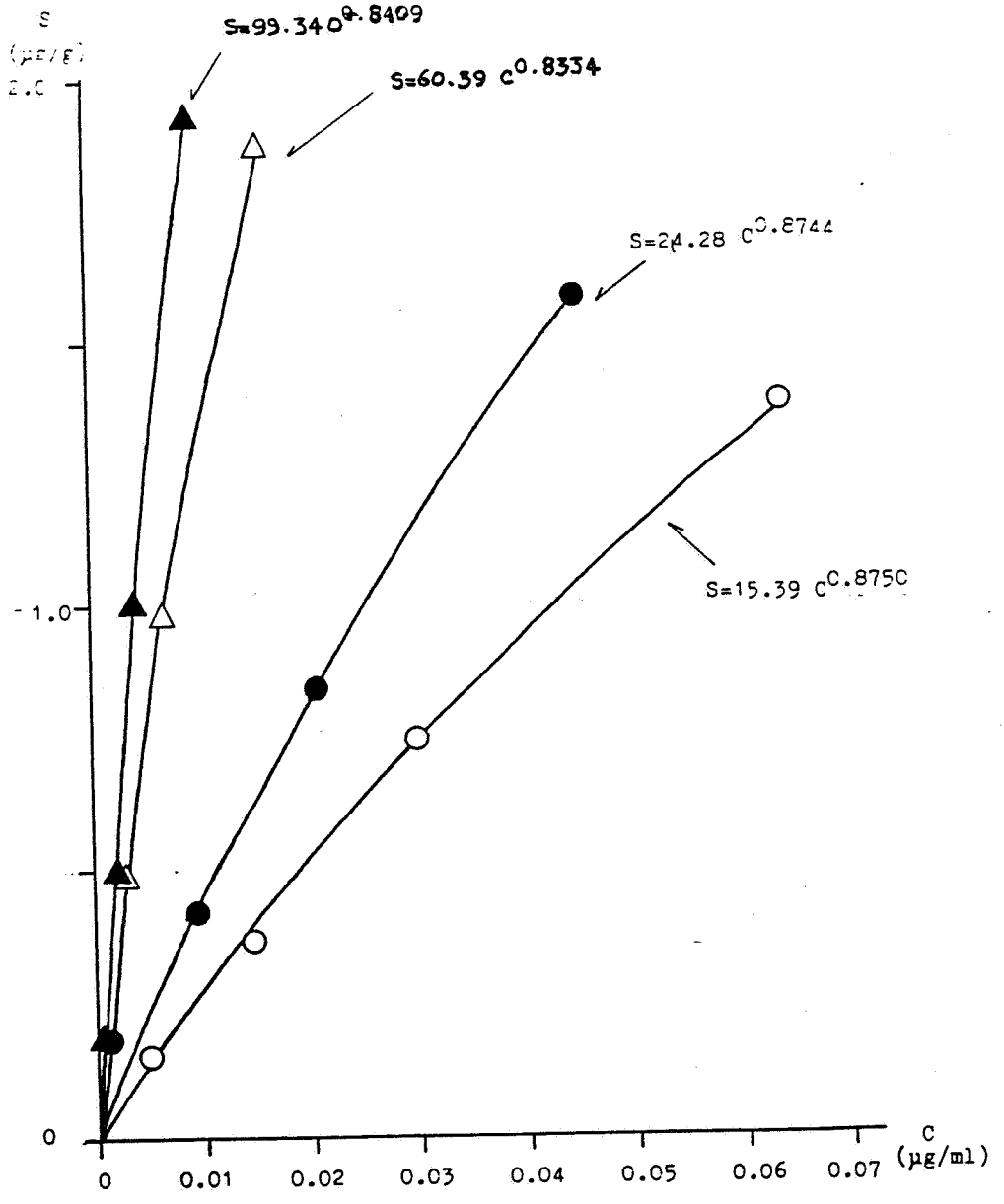

Fig.8 Equilibrium adsorption isotherms for NC-302.

▲ : Chiba soil ● : Gunma soil

△ : Nagano soil ○ : Aichi soil

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Table 26. Adsorption/Desorption Parameters for NC-302 and NC-302 Acid in Four Soils at 23°C

Soil type	NC-302						NC-302 Acid					
	Adsorption			Desorption			Adsorption			Desorption		
	K	1/N	Koc	K'	1/N'	Koc'	K	1/N	Koc	K'	1/N'	Koc'
Aichi	15	0.88	3078	313	1.76	62654	1.7	0.79	346	1.9	0.76	370
Gunma	24	0.87	1214	23	0.87	1158	4.2	0.79	212	6.5	0.80	326
Chiba	99	0.84	1948	11	0.87	2150	40	0.86	783	60	0.89	1171
Nagano	60	0.83	1024	66	0.88	1112	33	0.87	564	49	0.91	828

Table 29. Adsorption/Desorption Parameters for 2,4-D and DDT in Four Soils at 23°C

Soil type	2,4-D						DDT					
	Adsorption			Desorption			Adsorption			Desorption		
	K	1/N	Koc	K'	1/N'	Koc'	K	1/N	Koc	K'	1/N'	Koc'
Aichi	0.85	1.1	170	0.55	0.85	110	556	1.1	111240	524	0.99	104704
Gunma	1.2	1.0	58	2.2	1.0	112	548	1.0	27414	567	0.94	28351
Chiba	7.3	1.0	143	8.9	1.0	174	544	0.97	10666	2447	1.08	47982
Nagano	6.3	1.0	106	8.5	1.0	144	1245	1.1	21105	1110	1.00	18819

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Conclusions

The adsorption/desorption characteristics of NC-302 (DPX-Y6202) and its major metabolite NC-302 acid were determined and compared with reference materials.

Isotherms were applied to the Freundlich equation. Based on the adsorption coefficient values, the order of adsorption in the four soils was: DDT > NC-302>NC-302 acid >2,4-D. Comparing the desorption coefficient values, the order of desorption in the four soils was the reverse of adsorptivity.

The properties of these Japanese soils were not compared to those of American soils. Soils were not aged aerobically aged with NC-302 to allow for the formation of degradates of NC-302 other than NC-302 acid.

Registration and Application Information

Two emulsifiable concentrate formulations of Du Pont Assure® Herbicide to be used as a selective postemergence herbicide for the control of annual and perennial grasses in soybeans and cotton.

Assure® was evaluated under Experimental Use Permit numbers 352-EUP-114 (cotton) and 352-EUP-115 (soybeans) in 1984 and investigation under the same permits will continue in 1985. Efficacy data generated under the Experimental Use Permits and research testing has been compiled and is on file at Du Pont. The data generated thus far is to support the claims of labeling cited in Section B of their petition.

The 10% EC formulation is to be applied at 0.2-0.4 lb ai/A depending on regional rainfall. In arid regions Assure® should be applied soon after irrigation and a second application 2-3 weeks after emergence of new grass.

Executive Summary

Aqueous photolysis of DPX-Y6202 at pH 5 resulted in the formation of DPX-acid, phenol-1 and phenol-2 and non-polar unknowns with a half-life of approximately 55 days. Both phenols-1 and 2 were detected in quinoxaline-labeled samples, but only phenol-1 was reported among phenyl-labeled photoproducts. Major pathway for decomposition was by loss of CO_2.

Soil photodecomposition of DPX-Y6202 at 365 nm occurred with an estimated half-life of 30 days. Photoproducts were the same as in the aqueous experiment above only phenol-3 and no phenol-2 was reported. This was expected since only phenyl-[^{14}C]-DPX-Y6202 was used in this study. The major decomposition pathway involved the elimination of CO_2 from DPX-Y6202.

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Recommendations

Available data are insufficient to fully assess the environmental fate of DPX-Y6202. The submission of data relative to registration requirements is summarized below:

Photolysis

A. Aqueous

1) This study was scientifically valid.

2) Photolysis of pH 5 resulted in the formation of DPX-acid, phenols-1 and -2 plus polar intermediates with an estimated half-life of 55 days for DPX-Y6202.

3) Irradiation conditions, half-life estimates, material balances, identification of decomposition products which were produced fulfilled all necessary EPA requirements.

B. Soil

1) This study was scientifically valid.

2) Photolysis at 365 nm resulted in the formation of DPX-acid and phenol-3 with an estimated half-life of 30 days for DPX-Y6202.

3) EPA requirements were not fulfilled by this data since metabolites of concentration <0.01 ppm were not identified.

Aerobic Metabolism

1) This study was scientifically valid.

2) DPX-Y6202 was metabolized with a half-life of less than a day to DPX-acid which was further metabolized to phenols-1, 3, and 4 plus CO_2.

3) Aerobic conditions were specified, half-life estimates, residue decline curves, material balances, identification of metabolites were all provided according to EPA data requirements.

Soil Degradation

1) These studies were scientifically invalid due to the incompleteness of reported methods, and data.

2) Aerobic metabolism of DPX-Y6202 in Japanese soils resulted in similar degradation products to those found in american soils. DPX-acid produced was metabolized more slowly, both aerobically and anaerobically, in Japanese soils than in american soils.

3) Aerobic Metabolism: This study failed to meet guideline requirements since incubation temperatures was not provided, no attempts were made to ensure aerobicity of stored samples no residue decline curves were provided, and the experimental procedures were poorly described.

Anaerobic Metabolism: This study failed to meet guideline requirements for the same reasons as in the aerobic study above, in addition soils were not aged aerobically for 30 days prior to this study.

Sterile Samples: This study failed to meet guideline requirements because the data was limited, no proof of the maintenance of sterile conditions was offered, no CO_2 data was provided.

Anaerobic Aquatic Metabolism

1) This study was scientifically valid.

2) Anaerobic metabolism resulted in rapid (half-life ~1 day) conversion to DPX-acid which was further metabolized to phenols-1, 2, 4, and hydroxyphenol-2.

3) The registrants failed to identify unknown metabolites 1 and 2 which were present at >0.01 ppm as required by EPA guidelines.

Batch Equilibrium

1) This study was scientifically valid.

2) Freundlich adsorption isotherms indicated that DPX-Y6202 was strongly adsorbed onto four soils and to be Class 1 (immobile) by soil TLC.

3) This study failed to meet EPA requirements because adsorption/desorption data of DPX-Y6202, and comparisons with standard compounds satisfactorily established a mobility class for DPX-Y6202 only. Soils were not aged for 30 days and mobility was not determined for any of the DPX-Y6202 degradates.

Soil Mobility

1) This study was scientifically valid.

2) NC-302 (DPX-Y6202) was classified as immobile and NC-302 acid as low mobility based on soil TLC results on four Japanese soils.

3) This study does not meet requirements since the mobilities of NC-302 and NC-302 acid were established on four Japanese soils which were not aged aerobically for 30 days. The mobility of major metabolites other than NC-302 acid were not determined.

Adsorption/Desorption

1) This study was scientifically valid.

2) Batch equilibrium data for NC-302 and NC-302 established the mobility class of immobile, and slightly mobile, respectively. Mean Kom on four Japanese soil established an adsorbtivity order of DDT>NC-302> NC-302 acid >2,4-D.

3) This study did not satisfy EPA requirements because Japanese soils were not aged aerobically to allow for formation of NC-302 degradates.

REFERENCES

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3) Gibian, D.G., "DPX-Y6202 Experimentals Use Permit: Product Chemistry". E.I. dupont de Nemous and Co., Inc., Agri. Chem. Dept., Research Div., Document No. AMR-125-83, 4-18-83.