Degradation of 3-(3-chloro-4-chlorodifluoromethylthiophenyl)-1,1-dimethylurea (Clearcide®) in Paddy Soils

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The degradation of 3-(3-chloro-4-chlorodifluoromethylthiophenyl)-1,1-dimethylurea (Clearcide®) in paddy soils on which rice plants were planted under flooded conditions was investigated in accordance with growth stages of rice plants by using 14C-Clearcide labeled at 1,1-dimethyl and unlabeled Clearcide. At the end of the growth stage periods of rice plants, the soil was sampled and extracted with 80% acetonitrile and partitioned into organic, aqueous and unextracted fractions. Each fraction was subjected to radioactivity assay, tlc and glc.

More than 50% of radioactivity was detected in the chloroform soluble fraction even after the lapse of time and the activity in the water soluble fraction was negligible (maximum detected value was 2.7%). Detected compounds from the acetonitrile extracts were mainly parent Clearcide and small amounts of degradation products.

Desmethyl Clearcide and Clearcide sulfoxide and its sulfone were identified as major degradation products, and desmethyl Clearcide sulfoxide, its sulfone and aniline derivatives were also identified. Small amounts of three unknown degradation products were found with the lapse of time. Half life period of Clearcide in paddy soils was about 30 to 40 days.

INTRODUCTION

Clearcide® (code No. KUE 2079A) has been synthesized and screened as a herbicide by Bayer AG in West Germany and it is a new paddy herbicide being cooperatively developed by Bayer AG and Nihon Tokushu Noyaku Seizo K.K.1-4 It had been named as thiochlmethyl. It displays pre- and post-emergence efficacies on many kinds of broadleaf weeds and certain grasses in the paddy field.5 Clearcide can be used in soil incorporation and submerged application with good tolerance for transplanted and directly seeded rice. The fate and behaviour of the herbicide in paddy soil were reported.6 The fate of Clearcide which was applied to flooded soil by the submerged application after transplanting rice seedlings was studied. Absorption, translocation, accumulation and metabolism of Clearcide in the rice plants have been reported.7-9

The present paper describes the behaviour and the degradation of Clearcide in paddy soils under flooded conditions by using 14C-Clearcide labeled at methyl groups of 1,1-position and unlabeled Clearcide.

MATERIALS AND METHODS

1. Radioactive Clearcide

Universally 14C–labeled dimethylamine was added dropwise to 3-chloro-4-chlorodifluoro-
methylthiophenyl isocyanate in benzene at 10°C for 2 hr. After stirring for 3 hr at room temperature the precipitate was filtered off. The crude product was recrystallized from n-hexane and 14C-Clearcide was purified by tlc.

Its specific activity was 3.7 mCi/mmol and radiochemical purity was above 99%.

2. Clearcide and Its Degradation Products

The following non-radioactive authentic compounds were synthesized and purified in our laboratory. The chemicals used were listed in Table 1 along with their designations and thin layer chromatographic properties.

3-(3-Chloro-4-chlorodifluoromethylthiophenyl)-1,1-dimethylurea (C-2) was recrystallized with n-hexane and benzene from crude Clearcide supplied by Bayer AG. mp 115-116°C. The chemical purity of Clearcide was 99.5%. Anal. Calcd. for C10H10NSOSC12F2: C, 38.11; H, 3.20; S, 10.17. Found: C, 38.42; H, 3.17; S, 10.25.

3-(3-Chloro-4-chlorodifluoromethylsulfinylphenyl)-1,1-dimethylurea (C-4) was prepared from Clearcide by oxidation with m-chloroperbenzoic acid in chloroform solution. mp 93-94°C. Anal. Calcd. for C10H10N202SC12F2: C, 36.26; H, 3.04; S, 9.68. Found: C, 36.34; H, 3.05; S, 9.60.

3-(3-Chloro-4-chlorodifluoromethylthiophenyl)-1-methylurea (C-5) was synthesized by the following reaction.

\[
\text{CICH}_2\text{CICH}_2\text{CS}_{\text{C}_6\text{H}_3}\text{NCO} + \text{CH}_3\text{NH}_2 \rightarrow \text{CICH}_2\text{CICH}_2\text{NHCONCH}_3
\]

mp 163-165°C. Anal. Calcd. for C9H8N20SC12F2: C, 35.19; H, 2.98. Found: C, 35.06; H, 2.89.

3-Chloro-4-chlorodifluoromethylthioaniline (D-1) was prepared from 3-chloro-4-chlorodifluoromethylthiophenyl isocyanate by acid hydrolysis. mp 176-178°C. Anal. Calcd. for C10H10NSClF2: C, 34.44; H, 2.06. Found: C, 34.60; H, 2.16.

3-(3-Chloro-4-chlorodifluoromethylthiophenyl)urea (D-2) was synthesized by the following reaction.

\[
\text{3-Cl-4-FClC}_{\text{C}_6\text{H}_3}\text{NCO} + \text{NH}_2\text{H}_2\text{O} \rightarrow \text{3-Cl-4-FClC}_{\text{C}_6\text{H}_3}\text{NHCONH}_2
\]


3. Radioactivity Assay

Radioactivities of 14C-Clearcide and its degradation products were assayed by a Beckman LS-150 liquid scintillation spectrometer. For the radioactivity assay, aliquots of 0.1-1.0 ml of chloroform or water solution were mixed with 10 ml of a scintillator solution which consisted of 4.0 g of 2,5-diphenyloxazole (PPO) and 0.1 g of 1,4-bis-2-(5-phenyloxazolyl)benzene (POPOP) in 1,000 ml of toluene. Radioactivity in the soil was determined after wet combustion by Van Slyke's procedure modified by Mori.10,11 The resulting 14CO2 was absorbed by 1 ml of Beckman Soluene-100. Quenching due to water and chloroform in sample preparations was corrected by the external standard technique.

4. Thin Layer Chromatography (tlc)

Tlc was performed on plates coated with silica gel B-5F (Wako Pure Chem. Industries Ltd., 0.5 mm thick, 20 x 20 cm). A mixture of chloroform and acetone (9:1 v/v) was mainly used as a developing solvent and other solvent systems were also used. Rf values for example are shown in Table 1.

5. Gas Liquid Chromatography (Glc)

Gas chromatographic determination of Clearcide and its degradation products was carried out with a JGC-1100 gas chromatograph (Japan Electron Optics Lab., Tokyo) equipped
with an electron capture detector (63Ni) under the following conditions. Glc columns were pyrex glass column (i.d. 3 mm, length 120 cm) packed with 10% silicone DC 200 on Gas Chrom Q (60-80 mesh) and 5% silicone OV-101 on Gas Chrom Q (80-100 mesh). Column temperature was either 190°C or 150°C. Temperatures of the injection port and the detector were 270°C and 250°C, respectively. The flow rate of nitrogen (carrier gas) was 60 ml/min. For gas chromatographic quantitative determination of Clearcide, preparation by a bromination procedure was tried. Clearcide was hydrolyzed with sulfuric acid and brominated in one step. The resulting brominated derivative was determined by glc (ECD) using column packed with 5% silicone OV-1 on Gas Chrom Q, Column temperature was 180°C.6,12

Table 1 Rf values of Clearcide and its degradation products in tlc.

<table>
<thead>
<tr>
<th>Spot No.</th>
<th>Compounds</th>
<th>Rf in solvent system**</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-1</td>
<td>3-Cl-4-F2ClC=CH2-NH2</td>
<td>0.69 0.65</td>
</tr>
<tr>
<td>C-1</td>
<td>Unknown A</td>
<td>0.66 0.60</td>
</tr>
<tr>
<td>C-2</td>
<td>3-Cl-4-F2ClC=CH2-NHCON(CH3)2</td>
<td>0.55 0.37</td>
</tr>
<tr>
<td>C-3</td>
<td>3-Cl-4-F2ClC=CH2-NHCON(CH3)2</td>
<td>0.48 0.29</td>
</tr>
<tr>
<td>C-4</td>
<td>3-Cl-4-F2ClC=O-C6H4-NHCON(CH3)2</td>
<td>0.45 0.29</td>
</tr>
<tr>
<td>C-5</td>
<td>3-Cl-4-F2ClC=CH2-NHCON(CH3)</td>
<td>0.33 0.28</td>
</tr>
<tr>
<td>C-6</td>
<td>3-Cl-4-F2ClC=O-C6H4-NHCON(CH3)</td>
<td>0.24 0.17</td>
</tr>
<tr>
<td>C-7</td>
<td>3-Cl-4-F2ClC=O-C6H4-NHCON(CH3)</td>
<td>0.23 0.17</td>
</tr>
<tr>
<td>D-2</td>
<td>3-Cl-4-F2ClC=CH2-HCONH3</td>
<td>0.11 0.18</td>
</tr>
<tr>
<td>C-8</td>
<td>Unknown B</td>
<td>0.11 0.07</td>
</tr>
<tr>
<td>C-9</td>
<td>Unknown C</td>
<td>0.00 0.00</td>
</tr>
</tbody>
</table>

* See Fig. 2.
** Developing solvents; 1 Chloroform-Acetone (9:1 v/v), 2 n-Hexane-Acetone (2:1 v/v).

6. Soil Samples
Soils were taken from paddy fields at Hino shi in Tokyo, Chiba Agricultural Experiment Station in Chiba and Okegawa Agricultural Diffusion Station in Saitama in March of 1972 and stored at 3°C. The physico-chemical properties of the soils used are given in Table 2. The properties of paddy soils used in this experiment are common in Japanese rice fields.

7. Application of 14C-Clearcide and Sampling
Paddy soil (Hino in Tokyo) was crushed and passed through a 5 mm sieve. Each 1/2,000 are-sized Wagner’s round pot (25 cm in diameter × 30 cm deep) was filled with 7 kg of Hino soil in addition to 3 kg of sand and 4 kg of gravel in the bottom, to which 6 g of a compound fertilizer (N15-P15-K15) and 5 g of 20% super phosphate were applied. The soil was flooded with water up to 3 cm deep. No leaching of water from the bottom of the pot was allowed during the rice culture. About 20 days later, three bundles of three rice seedlings (Oryza sativa L., V. Nihonbare) at 2 to 3 leaf stage were transplanted to a pot and kept to grow further in a phytotron (temperature 28°C–35°C, humidity 70–80%). An emulsifiable concentrate of 10% Clearcide was prepared by mixing 14C-Clearcide, Sorpol 355 (emulsifier) and xylene in a weight ratio of 10:5:85. Three days after transplanting, 400 mg of the 10% Clearcide emulsifiable concentrate was diluted with 2 liter of water, and 200 ml of the diluted emulsion which contained 4 mg of 14C-labeled Clearcide (11.8 μCi, equivalent active ingredient 80 g/10 a) was added to the paddy water in a 1/2,000 are-sized Wagner’s pot and it was made to distribute evenly in the paddy water by stirring. Paddy water was kept 3 cm deep and the

Table 2 Properties of paddy soils used.

<table>
<thead>
<tr>
<th>Location</th>
<th>Origination texture</th>
<th>Clay content (%)</th>
<th>Organic matter (%)</th>
<th>C.E.C. (m.e./100 g)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hino in Tokyo</td>
<td>Alluvial clay loam</td>
<td>17.3</td>
<td>5.1</td>
<td>20.5</td>
<td>5.4</td>
</tr>
<tr>
<td>Okegawa in Saitama</td>
<td>Volcanic ash silty loam</td>
<td>6.3</td>
<td>15.2</td>
<td>35.9</td>
<td>5.9</td>
</tr>
</tbody>
</table>
plants were kept to grow in a phytotron until the harvest time.

The degradation of $^{14}$C-Clearcide in paddy soil and water was surveyed at various growth stages. $^{14}$C-Clearcide was applied once on the 10th of October, 1973, and harvest time was on the 15th of February, 1974. After the paddy water was transferred into a flask, whole plants of rice were sampled from the pots and washed with water to remove soil particles from roots. Then, soil samples up to the depth of about 10 cm were taken from six different places in a pot by a borer of 2.5 cm in diameter and the soil was mixed well with a spoon.

Soil samples were collected at 15 min, 10 hr, 1, 3, 7, 10 days (seedling stage), 32 days (tillering stage), 54 days (booting stage), 77 days (milk-ripening stage), 100 days (heading stage) and 150 days (20 days after harvest time) after application. Paddy water samples were collected at 15 min, 10 hr, 1, 3, 7 and 10 days.

8. Extraction and Analytical Methods for Paddy Soil and Water

Fifty grams of each paddy soil sample was blended with 200 ml of 80% acetonitrile for 30 min on a shaking machine and then filtered under vacuum. The residue was washed with acetonitrile and extracted again by blending with 80% acetonitrile for 30 min. After filtration all the filtrates were combined and evaporated on a vacuum rotary evaporator at 40-45°C to remove most acetonitrile. The remaining aqueous solution was transferred to a separatory funnel and partitioned with three 30 ml portions of chloroform. Aqueous phase was concentrated to a definite volume and radioactivity was measured. Chloroform phase was evaporated just to dryness and the residue was dissolved in 10 ml of chloroform for tlc and glc.

An aliquot of 0.1–1.0 ml of the chloroform soluble fraction was applied on a silica gel plate (20×20 cm). Clearcide and its degradation products were separated by tlc using mainly a mixture of chloroform and acetone (9 : 1 v/v) as a developing solvent (Table 1). For comparison, authentic compounds of Clearcide and its degradation products were spotted on both sides of the plate. After developing, the chromatographed plate was exposed to an X-ray film to make a radioautograph. The spots of reference compounds were detected by irradiation of ultraviolet rays, and the radioactive Clearcide and its degradation products were detected by radioautograms on X-ray film. The radioactive spots on the tlc were located by referring to the radioautogram.

The radioactive spots of their corresponding zones were eluted with methanol from silica gel and their radioactivity was counted with a liquid scintillation spectrometer. After measuring all the extracts were evaporated to remove most solvent and the remaining solution was subjected to glc as described above. Then, the residues of fractions of C-2 and C-5 isolated by tlc were dissolved in benzene and methylated with methyl iodide and sodium hydride in dimethyl sulfoxide according to the method of J. F. Lawrence. The reaction scheme for the methylation of the compounds is shown for Clearcide. After the N-methylation these phenyl ureas were subjected to GC–mass spectrometry (Shimadzu–LKB 9000) column packed with 2% silicone OV–1 on Chromosorb W (60–80 mesh). The column temperature was isothermal at 200°C.

One hundred milliliters of each mixed paddy water sample was extracted twice with 100 ml of chloroform by shaking. After combination the chloroform extract was concentrated and radioactivity was determined by the same procedure as described above.

Radioactivity in residual soil was measured by Van Slyke procedure modified by Mori.

9. Application of Unlabeled Clearcide and Its Analytical Method

Chiba soil and Okegawa soil were screened through a 2 mm sieve. Ten grams (oven dried weight basis) of each soil sample was transferred into a 30 ml glass jar and the soil sample was flooded with water up to
about 1 cm deep. Purified non-radioactive Clearcide was dissolved with acetone to be 30 ppm solution. One half milliliter of the Clearcide solution were added at the concentration of 1.5 ppm on dry soil basis. The soil was thoroughly mixed using a glass rod and the soil remaining on the glass rod was rinsed into a glass jar with a small amount of water. Each glass jar was covered with a sheet of aluminium foil with several small holes. These soil samples were incubated in a dark chamber at 28°C with humidity of 90–100%. Water was supplied to maintain the water depth during the experiment. Soils were sampled at 1, 3, 10, 21, 42, 72 and 100 days after treatment. Each soil was blended with 50 to 100 ml acetone for one hour on a shaking machine and then filtered under vacuum. The acetone was evaporated on a rotary evaporator at 40–45°C. After adding 100 ml of 10% sodium chloride solution, the aqueous solution was extracted three times with 50 ml of n-hexane. Combined n-hexane was concentrated and partitioned with 80% acetonitrile and n-hexane. The acetonitrile layer was evaporated to dryness and the residue was dissolved in about 1 ml of acetone for TLC. Then, the residual acetone solution of soil extracts was cleaned up by TLC as above. The absorbent of the corresponding zone (Clearcide) was scraped off from the plate and extracted with methanol for GLC. The methanol solution was evaporated and brominated, and the derivative was determined by GLC (ECD) as described above.

RESULTS AND DISCUSSION

1. Behaviour of 14C-Clearcide in Paddy Soil and Water at Rice Seedlings

The distribution of radioactivity extracted with 80% acetonitrile in paddy soil and water under flooded conditions is shown in Fig. 1. Paddy soil and water were collected from the Wagner’s pots and analyzed at 15 min, 10 hr, 1, 3, 7 and 10 days after application. Acetonitrile extracts from soil were concentrated and the remaining aqueous solutions were partitioned with chloroform. Immediately after treating the radioactive Clearcide, more than 98% of the radioactivity was recovered from water.

However, the radioactivity in water rapidly decreased, and the amount of radioactivity in soil increased with decreasing the amount in water. The radioactivity in soil reached a level of more than 50% of the applied radioactivity one day after treatment, and rapidly increased with the lapse of time. When 14C-Clearcide was applied to the paddy water at the seedling stage, 7 days after the treatment most of the radioactivity appeared in the soil. However, acetonitrile extractable radioactivity gradually decreased in soil with the time. When acetonitrile extracts were partitioned with chloroform and water, most of the radioactivity appeared in the chloroform soluble fraction. Water soluble radioactivity contained only less than 2% of the applied one. The radioactive materials in the chloroform soluble fraction from the soil were identified with authentic compounds by co-chromatography using TLC and GLC. The radioactivity in the chloroform soluble fraction was mainly due to Clearcide and the radioactivity of the degradation products was minor (Table 4).

Takase reported that adsorption and desorption of herbicides were compared in various paddy soils under flooded conditions after soil incorporation treatment, and Clearcide was adsorbed much more rapidly in Okegawa soil than in Hino soil or Chiba
soil. These results indicated that the adsorption of Clearcide in the soils was largely affected by organic matter content and cation exchange capacity of paddy soil used. Then, Takase reported that about 80% of the applied Clearcide to a clay loam paddy soil appeared in the surface layer up to 2 cm deep in 3 days after submerged application, and very small amounts were found in the lower layer (2–10 cm deep). When \(^{14}\text{C}\)-Clearcide was added to paddy water in a 1/2,000 are-sized Wagner’s pot, the decrease of radioactivity in water was rapid and a large amount of radioactivity was found in the soil. From this finding it was presumed that Clearcide was adsorbed rapidly on soil particles after treatment. The radioactivity in soil and water was largely due to parent compound within 10 days after treatment. The radioactivity in the water soluble fraction was very small compared with that in the chloroform soluble fraction.

2. Fate of Clearcide in Paddy Soil

Changes in the radioactivity of each fraction in soil after the seedling stage application are shown in Fig. 2. Acetonitrile extracts of soil were concentrated and partitioned with chloroform. Table 3 shows the rate of distribution in chloroform soluble, water soluble and unextractable fractions of the soil after treatment. When rice plants were kept growing in a phytotron after submerged application of the chemical, the total radioactivity in soil gradually decreased with the lapse of time. Then, the radioactivity of acetonitrile extracts from the soil decreased also with the time. About 40% of the applied radioactivity disappeared within 77 to 100 days of treatment under the flooded conditions.

The persistence of phenyl substituted urea herbicides in soils was investigated by a number of workers. Leaching by rainfall and irrigation water, adsorption to soil particles, volatilization, photodecomposition, chemical decomposition, microbiological degradation and plant uptake represent possible modes of phenylurea herbicide disappearance from soil. Hill et al. observed the evolution of \(^{14}\text{C}\)CO\(_2\) after adding \(^{14}\text{C}\)-Monuron labeled at methyl group to a clay loam soil under upland conditions and after 90 days about 10% of the applied radioactivity was recovered as \(^{14}\text{CO}_2\). About 40% of the applied radioactivity was liberated as \(^{14}\text{CO}_2\) within 24 hr after administration when \(^{14}\text{C}\)-Clearcide labeled at 1,1-dimethyl was orally administered to male rat at a rate of 10 mg/kg of body weight. The pots were kept in a phytotron, and rice plants in the pots were allowed to grow under submerged conditions after submerged application of \(^{14}\text{C}\)-Clearcide.

### Table 3 Distribution of radioactivity in soil after submerged application of \(^{14}\text{C}\)-Clearcide.

<table>
<thead>
<tr>
<th>Fractions</th>
<th>Concentration (dpm/g-wt) and percent of distribution of (^{14}\text{C})</th>
<th>Days after application</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>Total radioactivity*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chloroform soluble fr.</td>
<td>96.0**</td>
<td>91.0</td>
</tr>
<tr>
<td>Water soluble fr.</td>
<td>1.6</td>
<td>2.7</td>
</tr>
<tr>
<td>Unextracted</td>
<td>2.4</td>
<td>6.3</td>
</tr>
</tbody>
</table>

* dpm/g dry wt. soil. 33,000 dpm/g is equivalent to initial radioactivity applied.

** Figures indicate the percentage of radioactivity in each fraction of the total recovered.
ditions. Temperature, humidity and length of day-time were regulated to suitable conditions. Although applied $^{14}$C-Clearcide was taken up by the rice plants, the disappearance of the radioactivity from soil was thought to be mainly due to the release of $^{14}$CO$_2$ deriving from $^{14}$C-Clearcide labeled at 1,1-dimethyl group by chemical and microbial degradation.

On the other hand, the amounts of acetonitrile unextractable radioactive materials in the soil increased with the time. Thirty-two days after treatment with $^{14}$C-Clearcide, unextractable radioactive materials reached a level of about 30% of the total radioactivity in soil. With the lapse of time, unextractable radioactivity increased to a level of more than 50% of the radioactivity at 150 days after treatment. The unextractable radioactivity in soil could not be extracted with methanol or chloroform-methanol (9:1 v/v) by a Soxhlet extractor.

From these results, it was presumed that the radioactivity remaining in soil might be due to the formation of soil-bound residue which was not easily recovered from soil.

As shown in Table 3, most of acetonitrile extractable radioactivity was found in the chloroform soluble fraction. After partition with chloroform, the radioactivity of water soluble fraction was detected slightly during the course of experiment. The radioactive products in the chloroform soluble fraction were detected by autoradiogram after thin layer chromatography as shown in Fig. 3. Distribution of radioactivity in the chloroform soluble fraction is shown in Table 4. The parent Clearcide was the main compound present in the chloroform extracts until the harvest time, and the degradation products were present only in small amounts.

As shown in Fig. 2, the degradation of parent Clearcide extracted with acetonitrile in soil gradually decreased with time, and its half life period was about 37 days.

![Fig. 3 Thin-layer chromatograms showing separation of $^{14}$C-Clearcide and its degradation products in soil after $^{14}$C-Clearcide application. Developing solvent; CHCl$_3$-(CH$_3$)$_2$CO (9:1 v/v)](image)
In the laboratory experiment, the degradation of Clearcide in two types of paddy soils under flooded conditions were compared with each other using non-radioactive Clearcide. The progress of degradation of Clearcide extracted with acetone in Chiba soil and in Okegawa soil is shown in Fig. 4. The physico-chemical properties of paddy soils used in this experiment are shown in Table 2. The degradation rate of Clearcide was a little more rapid in Okegawa soil (volcanic ash silty loam) than in Chiba soil (alluvial loam). Under flooded conditions, the rate of disappearance of Clearcide in two types of paddy soils diminished gradually with the lapse of time, and the half life periods of Clearcide in Chiba soil and in Okegawa soil were about 40 and 32 days, respectively.

Although two soils were different in organic matter content and other properties, the degradation rates of Clearcide in two soils showed similar patterns. Additionally, the degradation rates in soils under flooded conditions were compared between greenhouse and laboratory experiments. As shown in Fig. 2 and Fig. 4, although given conditions and soils were different, the degradation rates of Clearcide in both soils were observed approximately similar. Furthermore, significant difference in the half life period of Clearcide was not observed between greenhouse and laboratory experiments.

### Table 4 Relative amounts of $^{14}$C-Clearcide and its degradation products in the chloroform soluble fraction extracted with 80% acetonitrile in soil.

<table>
<thead>
<tr>
<th>Compounds*</th>
<th>Amounts (% of the radioactivity in CHCl$_3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Days after appl. 3</td>
</tr>
<tr>
<td>C-1</td>
<td>1.4</td>
</tr>
<tr>
<td>C-2</td>
<td>95.3</td>
</tr>
<tr>
<td>C-3+C-4</td>
<td>0.8</td>
</tr>
<tr>
<td>C-5</td>
<td>1.6</td>
</tr>
<tr>
<td>C-6+C-7</td>
<td>0.2</td>
</tr>
<tr>
<td>C-8</td>
<td>0.3</td>
</tr>
<tr>
<td>C-9</td>
<td>0.2</td>
</tr>
</tbody>
</table>

* See Table 1 and Fig. 2.

![Degradation of Clearcide in two different soils.](image)

In the laboratory experiment, the degradation of Clearcide in two types of paddy soils under flooded conditions were compared with each other using non-radioactive Clearcide. The progress of degradation of Clearcide extracted with acetone in Chiba soil and in Okegawa soil is shown in Fig. 4.

The physico-chemical properties of paddy soils used in this experiment are shown in Table 2. The degradation rate of Clearcide was a little more rapid in Okegawa soil (volcanic ash silty loam) than in Chiba soil (alluvial loam). Under flooded conditions, the rate of disappearance of Clearcide in two types of paddy soils diminished gradually with the lapse of time, and the half life periods of Clearcide in Chiba soil and in Okegawa soil were about 40 and 32 days, respectively.

### 3. Degradation of Clearcide in Paddy Soil

On thin layer chromatograms of acetonitrile extracts 9 radioactive spots were found, as shown in Fig. 3. The chloroform soluble fraction from the acetonitrile extracts in soil was characterized by tlc, glc and GC-MS. These degradation products were extracted from the tlc plate and identified by co-chromatography with authentic compounds. The results obtained are shown in Table 4. The amount of parent Clearcide recovered from the paddy soil exceeded 85% of the total radioactivity in the chloroform soluble fraction at 77 days after treatment. The degradation products were detected in small amounts. However, the amount of C-5 increased to about 15% of the chloroform soluble fraction 100 to 150 days after treatment. For identification, C-5 was extracted with methanol from the silica gel plate ($R_f$ value: 0.33) and methylated with methyl iodide and sodium hydride in dimethyl sulfoxide.
oxide. The mass spectrum of methylated product of C-5 revealed a molecular ion peak at m/e 328 (M⁺), and peaks at m/e 293 (M⁺−Cl), m/e 284 (M⁺−N(CH₃)₂), m/e 243, and m/e 171 (shown in Fig. 5). GC–MS was conducted with this degradation product methylated with sodium hydride and methyl iodide. The retention time and mass spectrum of methylated product of C-5 coincided with the authentic standard compound 3-(3-chloro-4-chlorodifluoromethylthiophenyl)-1,1,3-trimethylurea. Therefore, the major degradation product in the chloroform soluble fraction was identified as 3-(3-chloro-4-chlorodifluoromethylthiophenyl)-1-methylurea. Four related degradation products were identified by co-chromatography with tic and glc as 3-(3-chloro-4-chlorodifluoromethylsulfinylphenyl)-1,1-dimethylurea (C-4), 3-(3-chloro-4-chlorodifluoromethylsulfonylphenyl)-1,1-dimethylurea (C-3), 3-(3-chloro-4-chlorodifluoromethylsulfenylphenyl)-1-methylurea (C-7) and 3-(3-chloro-4-chlorodifluoromethylsulfenylphenyl)-1-methylurea (C-6). However, these oxidized degradation products in the soil were less than 5% of the applied amount of Clearcide.

Two non-radioactive spots (D-1 and D-2 in Table 1) in the acetonitrile extracts were extracted with methanol from a silica gel plate and identified by glc with authentic compounds. As a result of glc analysis by co-chromatography, each peak of these degradation products coincided with 3-chloro-4-chlorodifluoromethylthioaniline (D-2) and 3-chloro-4-chlorodifluoromethylthioaniline (D-1) and 3-(3-chloro-4-chlorodifluoromethylthiophenyl) urea (D-2). On thin layer chromatography of chloroform soluble fraction, unknown A (C-1), B (C-8) and C (C-9) were detected, as shown in Fig. 3 and Table 4. During the incubation period, radioactivity of three unknown fractions in the chloroform extracts was very small, only 1 to 2% even on 150 days.

4. Proposed Degradation Pathways

From these results, possible degradation pathways of Clearcide in paddy soils were proposed as shown in Fig. 6.

Demethylation and deamination-decarboxylation of phenyl urea herbicides in soil have been reported by a number of workers. It was presumed that the degradation of Clearcide in soil was initiated at demethylation, subsequent hydrolysis, and sulfoxidation to Clearcide sulfoxide and its sulfone. The first degradation pathway in paddy soil involves dealkylation to produce desmethyl Clearcide. Then, 3-(3-chloro-4-chlorodifluoromethylthiophenyl) urea (D-2) and 3-chloro-4-chlorodifluoromethylthioaniline (D-1) were produced in soil by hydrolysis of demethylated compound. Desmethyl Clearcide had less phytotoxicity compared with the parent compound.

Several organophosphorus pesticides in paddy soil under flooded conditions are known to undergo oxidation of thioether linkages to the corresponding sulfoxide and sulfone. Clearcide sulfoxide and its sulfone, the oxidation products of thioether linkage, were detected in soils under flooded conditions, but these
oxidized compounds were found only in a small percentage. However, with respect to Clearcide at least, the second possible degradation route involves oxidation of thioether linkage to Clearcide sulfoxide and its sulfone. These oxidized compounds were detected in the plants metabolism studies.\(^1\)\(^2\)\(^3\)

The presence of \(^14\)C-labeled monoalkyl products would suggest that Clearcide was degraded mainly via demethylation. No significant accumulation of monomethyl and other degradation products of Clearcide was found in this study.

**Fig. 6** Proposed degradation pathways of Clearcide in soils.

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