Degradation of the Herbicide Halosulfuron-methyl in Two Soils under Different Environmental Conditions*

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A laboratory experiment was conducted to study the degradation of the herbicide halosulfuron-methyl (NC-319) in Anjo (kaoline) and Nagano (montmorillonite) soils in the controlled environment of soil moisture, pH and temperature regime. In one experiment, four levels of moisture contents (10 to 200% of maximum water holding capacity (MWHC)) and four temperature levels (4 to 30°C) were applied. In the other experiment, pH of the two soils were adjusted to ca. 5-9, being maintained at 50% MWHC and 25°C. The dissipation followed first-order kinetics in all cases. In the two soils, halosulfuron-methyl was dissipated faster with increasing the temperature and lowering the soil pH. However, increasing moisture contents increased the dissipation rate of halosulfuron-methyl in Anjo soil but not in Nagano soil.

INTRODUCTION

Study on the fate of pesticides in the environment is necessary both for agricultural practice and environmental safety. The dissipation of herbicides in soil is influenced by many chemical, physical, and biological processes. It is also governed by various soil properties, such as soil type, kind and content of clay minerals, organic matter content, pH, cation exchange capacity (CEC), soil texture, redox potential, moisture content and soil temperature.

Halosulfuron-methyl is a pyrazole sulfonylurea herbicide developed by Nissan Chemical Industries, Ltd. This herbicide is currently being evaluated for selective broadleaf postemergence weed control in upland fields. As a new developed herbicide, therefore, a clear understanding about the fate, persistence, and behavior of this chemical in the soil is essential for its proper use.

This research was aimed to determine the effect of soil conditions on the degradation process of halosulfuron-methyl, using two soils with different soil type and clay minerals. Under laboratory conditions, the degradation of halosulfuron-methyl under different soil-water content and temperature regime was examined. The effect of soil pH on the rate of degradation in both soils was also studied.

MATERIALS AND METHODS

1. Chemical

Analytical grade of halosulfuron-methyl [NC-319, methyl 3-chloro-5-(4,6-dimethoxypyrimidin-2-ylcarbamoylsulfamoyl)-1-methylpyrazole-4-carboxylate] (the purity, 99.8%; mp 175.5-177.2°C) was supplied by Nissan Chemical Industries, Ltd.

2. Apparatus

The HPLC system (Shimadzu) was composed of a LC-6A compressor leachate and a SPD-6A UV detector using an Inertsil ODS-2 column (4.6 mm i.d. × 25 cm, Shimadzu). A mixture of acetonitrile/methanol/water/phosphoric acid (500 : 100 : 500 : 1, by volume) was used as the mobile phase at a flow rate of 1.0 ml/min. The injection sample volume was 20 μl and UV 254 nm was used for monitoring.

3. Soil Samples

Two soil samples, Anjo and Nagano soils, were used.
in the experiments. Anjo soil is a diluvial soil of kaolinite clay mineral, and Nagano soil is an alluvial soil of montmorillonite clay mineral. Undried soil samples were crushed and passed through a 2 mm sieve prior to use.

The characteristics of these soils were as follows: Anjo soil: mineral soil with kaolinite clay, clay loam, clay content 38.4%, pH 6.5, total carbon (T-C) 1.24%, total nitrogen (T-N) 0.12%, CEC 9.50 mEq/100 g, MWHC 54.6%; Nagano soil: mineral soil with montmorillonite clay, silty clay loam, clay content 37.5%, pH 6.1, T-C 1.35%, T-N 0.17%, CEC 14.7 mEq/100 g, MWHC 75.5%.

4. Soil Conditions
For degradation of the herbicide under controlled environment conditions, four levels of moisture content and four levels of temperature regime which were 10, 50, 80 and 200% of MWHC and 4, 15, 25 and 30°C were applied in Anjo and Nagano soil, respectively. Undried soil of 20 g as dry weight soil basis was placed to 100 ml Erlenmeyer flasks. For moisture conditioning, water was added to each flask tailoring to its need. Then, each flask was covered with aluminum foil and preincubated in the dark for two weeks at designated temperature. Water was weekly added to the soil to maintain the designated moisture content throughout the course of the experiment.

For pH study, the soil pH was adjusted to ca. 5.0-9.0 by adding the appropriate amount of HCl or Ca(OH)₂ by usual procedure. The soils were maintained at 50% MWHC and 25°C.

5. Application of Halosulfuron-methyl and Incubation
Twenty micrograms halosulfuron-methyl (equivalent to 1 ppm on dry soil basis) was added to the preincubated soil and mixed well using a glass rod and hand shaking. Then, the soil was incubated under the same conditions as preincubation. The residual amounts of the chemical in the soil were analyzed after the designated periods.

6. Extraction and Purification
Two replications were sacrificed at intervals corresponding to 0, 7, 14, 21, 28, 35 and 45 days after treatment. The soil extraction method was informed by Nissan Chemical Industries, Ltd. (H. Igarashi and H. Yoshida, personal communication), but slightly modified. At appropriate intervals, the incubated soil was transferred to a 300 ml Erlenmeyer flask and extracted with 45 ml of a mixture of acetonitrile and water (4:1, v/v), 5 g of Celite and 5 ml of 6% phosphoric acid. The flask was sealed with parafilm and aluminum foil and shaken for 30 min by a mechanical shaker, then the mixture was filtered with suction. Residue in the flask was washed with 50 ml of acetonitrile/water (4:1, v/v) and the filtrate was combined. The extraction procedure was repeated again for the residue using 50 ml acetonitrile/water (1:1, v/v) and the combined filtrate was concentrated below 40°C to about 70 ml under a reduced pressure. After adjusting to pH 2, the concentrate was transferred to a 100 ml cap mes cylinder and filled up to the volume with water.

A 50 ml portion (corresponding to about 10 g of the soil sample) was taken and flowed into BOND ELUTE C₁₈ Cartridge. After passing the washing solution through the cartridge, the halosulfuron-methyl eluent in 5 ml acetonitrile was collected. The eluent was concentrated below 40°C to about 1 ml and then gently air-streamed until only the residue left.

The residue was dissolved in 10 ml of hexane/ethyl acetate (9:1, v/v) by sonication. Then, a 5 ml portion which corresponding to 5 g of soil sample was flowed into BOND ELUTE 2OH Cartridge. After passing the washing solution through the cartridge, the halosulfuron-methyl eluent in 5 ml of hexane/ethyl acetate (7:3, v/v) was collected. Similar concentration procedure as that on BOND ELUTE C₁₈ was done. The residue was dissolved in 2.5 ml acetonitrile and analyzed by HPLC.

Recovery of halosulfuron-methyl from Anjo and Nagano soils for time-zero samples averaged 94%.

7. Calibration
A standard plot of peak area vs. nanogram of halosulfuron-methyl was used for the determination of the amounts of the compound. The plot was linear over the range 2-800 ng injected.

8. Data Analysis
Rate of halosulfuron-methyl degradation in soil was calculated using first-order kinetics:

\[ C_t = C_0 e^{-kt} \]

where \( C_t \) is the halosulfuron-methyl concentration as a function of time in days (t), \( C_0 \) is the halosulfuron-methyl concentration at time 0, and \( k \) is the degradation rate constant. The degradation rate constant was calculated by linear regression from the transformed first-order rate equation, \( \ln C_t = \ln C_0 - kt \). The time when 50% of halosulfuron-methyl had degraded (\( T_{1/2} \)) was calculated from the equation \( T_{1/2} = 0.693/k \).

RESULTS AND DISCUSSION

1. Effect of Controlled Environment: Soil-Water Content and Temperature Regime
Residual halosulfuron-methyl concentrations were fit to first-order kinetic models using non-linear regression procedures. Rates of disappearance of halosulfuron-methyl under various moisture content and temperature regimes in Anjo and Nagano soils are presented in Figs.
At the end of 45 days, almost all of halosulfuron-methyl had disappeared from Anjo and Nagano soils with high moisture contents and/or high temperature. However, in the Nagano soil, the degradation proceeded regardless of moisture contents. In comparison to another sulfonylurea herbicide, chlorsulfuron, Walker and Brown\(^6\) reported that under British field conditions less than 1% of chlorsulfuron initially applied remained after 12 months. It has been widely reported that soil-water content and temperature significantly affected degradation rates of sulfonylurea herbicides\(^6-11\) and many other chemicals.\(^{12, 13}\) Increased soil moisture and temperature decreased chlorsulfuron persistence.\(^6, 11, 14, 15\) High soil-water content and high temperature may favor the herbicide loss through increased microbial activity.

The kinetic analysis of soil-water content and temperature regime data indicated that the degradation rates could be described by first-order kinetics. First-order rate constants \((k)\) and calculated half-life values are presented with 95% confidence intervals (Table 1). A plot of logarithm concentrations vs. time was linear; with highly significant \((p: 0.01)\) linear correlation coefficients ranged from 0.89 to 0.97 and from 0.93 to 0.99 for Anjo and Nagano soils, respectively. There was an exception where Nagano soil in 50% MWHC at 15°C was only significant at \(p: 0.05\) with linear correlation coefficient of 0.74 (data not shown). Half-life values calculated from the data ranged from 7.4 days under flooded conditions (200% MWHC) at 25°C to 91 days under upland conditions (50% MWHC) at 4°C and from 18 days under flooded at 25°C to 98 days under upland conditions at 4°C for Anjo and Nagano soils, respectively. Hence, halosulfuron-methyl degraded faster under flooded than upland conditions as well as under high than low temperature regime.

The degradation rates of halosulfuron-methyl across all soil-water content at 25°C and across all temperature at 50% MWHC are shown in Figs. 1 and 2. Across all moisture content at 25°C, half-life values were ranged from 7.4 to 26.5 days in Anjo soil and from 18.4 to 28.4 days in Nagano soil (Table 1) resulting that halosulfuron-methyl degraded faster in Anjo than Nagano soil.
These results conform to our adsorption data\(^{16}\) that Nagano soil adsorbed halosulfuron-methyl more strongly as compared to that Anjo soil which were shown with high Freundlich parameters, \(K_f\) and \(1/n\) values in Nagano soil. The redox potentials data also confirmed the results in which the redox potentials of the soils monitored during the study decreased faster in Anjo than Nagano soil (data not shown).

At the end of 45 days, it had only approximately 0.2 to 0.3 \(\mu g/g\) soil of halosulfuron-methyl in 10% to 80% MWHC, 0.03 \(\mu g/g\) soil in flooded (200% MWHC) soil at 25°C in Anjo soil, and about 0.2–0.3 \(\mu g/g\) soil across all moisture contents at 25°C in Nagano soil. In flooded soil halosulfuron-methyl was degraded 3–4 times faster than in 10% MWHC (air-dry soil) in Anjo soil. It could be explained with the findings by Fuesler and Hanafey\(^{17}\) in which chemical hydrolysis of the sulfonylurea moiety is the primary mode of degradation in air-dry soil, while microbial degradation and chemical hydrolysis both occur in flooded soil.

Across all temperature at 50% MWHC, on the other hand, decreasing temperature from 30 to 4°C decreased the degradation rates of halosulfuron-methyl in both soils with half-life values ranged from 13 to 91 days in Anjo soil and from 19 to 98 days in Nagano soil. Half-lives for 4 and 15°C were by extrapolation. Oppong and Sagar\(^{18}\) found that the degradation of triasulfuron was much faster at 30°C than at 10°C. The results showed a similar pattern with soil-water content study above in which halosulfuron-methyl was degraded more rapidly in Anjo than Nagano soil. At 4 and 15°C, moreover, halosulfuron-methyl was quite persistent and the degradation rate pattern was almost similar for both soils.

2. Effect of Soil pH

The rates of disappearance of halosulfuron-methyl at different pH values of Anjo and Nagano soils are shown in Fig. 3 and Table 2. In Anjo soil, the degradation rates of halosulfuron-methyl decreased as pH increased from 5.2 to 7.6 then somewhat increased as pH raised to more than 8.2; in Nagano soil, increasing soil pH generally decreased degradation rates of halosulfuron-methyl but the effect was not so remarkable. Peterson and Arnold\(^{19}\) observed that less persistence of chlorsulfuron occurred in the soils with pH of less than 5.5 than those near 7. When soil pH is greater than 7.5, degradation of chlorsulfuron is restricted which can lead to slow rates of loss.\(^{11, 20}\) Degradation of chlorsulfuron was also enhanced at acid pH.\(^{11, 14, 20–22}\) Halosulfuron-methyl was degraded in a markedly rapid rate when pH of Anjo soil was adjusted to 5.2 and 6.1. It was likely that those pHs settle the conditions favor to enhance the activity of halosulfuron-methyl degrading microorganisms, as Corbin and Upchurch\(^{23}\) suggested that the maximum rate of
degradation would occur at pH levels favorable for growth of the specific microorganisms for degradation of the chemical.

The degradation rate of halosulfuron-methyl was pH dependent and followed first-order kinetics. First-order rate constants \( k \) and calculated half-life values are presented with 95% confidence intervals (Table 2). Plots of logarithmic concentrations vs. time were linear (Fig. 3) with highly significant correlation coefficients (Table 2). Half-life values calculated from the data were ranged from 18 to 61 days and from 34 to 48 days for Anjo and Nagano soil, respectively. These results were comparably close to the calculated half-lives of chlorsulfuron on soils with pHs 6.2-8.1 which were 33 to 99 days, as reported by Thirunarayanan et al.\textsuperscript{11} Palm et al.\textsuperscript{8} also found that half-life of chlorsulfuron in the soil was between 30 and 60 days with its persistence affected by soil pH.

Half-lives of halosulfuron-methyl in Anjo and Nagano soils were shorter at low pH (6 and below) than at high pH (above 7). However, when comparing the half-life between the two soils, the half-lives were shorter in Anjo soil than in Nagano soil at low pH and vice versa at high pH suggesting that soil type may affect the degradation of herbicide in the soil.

In summary, the rate of degradation of halosulfuron-methyl in soils are dependent upon soil type, soil pH, temperature and soil moisture content. The degradation rate of halosulfuron-methyl in soil followed first-order kinetics. Apparently, environmental conditions such as soil-water content, temperature and soil pH favoring the chemical hydrolysis and activity of microbial degradation increase the dissipation of the herbicide. Increasing the temperature and lowering the soil pH increased the degradation rate of halosulfuron-methyl in Anjo and Nagano soils. Moreover, increasing moisture contents increased the degradation rate of halosulfuron-methyl in Anjo soil and thereabouts decreased in Nagano soil.

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Table 2 Effect of pH on the degradation rate of halosulfuron-methyl in Anjo and Nagano soils.

<table>
<thead>
<tr>
<th>Site</th>
<th>Adjusted pH</th>
<th>( k )</th>
<th>Half-life (days)</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CI</td>
<td>Predicted CI</td>
<td>+ CI</td>
</tr>
<tr>
<td>Anjo</td>
<td>5.2</td>
<td>0.051</td>
<td>-0.039</td>
<td>-0.027</td>
</tr>
<tr>
<td></td>
<td>6.1</td>
<td>0.037</td>
<td>-0.030</td>
<td>-0.024</td>
</tr>
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<td></td>
<td>7.6</td>
<td>0.019</td>
<td>-0.011</td>
<td>-0.004</td>
</tr>
<tr>
<td></td>
<td>8.2</td>
<td>0.018</td>
<td>-0.012</td>
<td>-0.007</td>
</tr>
<tr>
<td></td>
<td>9.5</td>
<td>0.020</td>
<td>-0.015</td>
<td>-0.010</td>
</tr>
<tr>
<td>Nagano</td>
<td>5.2</td>
<td>0.025</td>
<td>-0.021</td>
<td>-0.016</td>
</tr>
<tr>
<td></td>
<td>6.3</td>
<td>0.023</td>
<td>-0.018</td>
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<tr>
<td></td>
<td>7.2</td>
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<td>9.5</td>
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\( k \), first-order rate constant based on first order dissipation model; \( R^2 \), regression coefficient for first order fit; CI, 95% confidence intervals. * and **, significantly different at \( p<0.05 \) and \( p<0.01 \), respectively.

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Fig. 3 The effect of soil pH on the degradation of halosulfuron-methyl in (A) Anjo and (B) Nagano soils.
suggestions and help during the course of this study. Thanks are also due to Dr. H. Igarashi and Mr. H. Yoshida of Nissan Chemical Industries, Ltd. for supplying authentic chemicals and giving us the information on the analytical procedure. We are also deeply indebted to Dr. I. Goto of Soil Science Laboratory of our University for allowing us to use his laboratory facilities.

REFERENCES


要約

2種類の土壤を用いた異なる環境条件下における除草剤ハルスルフォメチルの分解

Dermiyati，銀塚昭三，山本 出

除草剤ハルスルフォメチル（NC-319）の土壤中の分解について安定・長野両土壌を用い，土壤の水分，pH，温度を変えて室内実験により研究した。水分は最大容水量の10～200%で4段階，温度は4～30℃で4段階で実験した。また，2土壌でpH約5～9，最大容水量50，25℃で実験した。すべての場合, 分解は一次反応に従った。土壤水分および温度が下がるにつれ，分解は速くなった。低pHで分解は速かった。分解速度は長野土壌より安定土壌のほうが速かった。