

# Relationships between Soil Properties and Sorption Behavior of the Herbicide Halosulfuron-methyl in Selected Japanese Soils\*

Dermiyati, Shozo KUWATSUKA and Izuru YAMAMOTO

Department of Agricultural Chemistry, Tokyo University of Agriculture,  
Setagaya-ku, Tokyo 156, Japan

(Received December 3, 1996; Accepted July 14, 1997)

The sorption of a sulfonylurea herbicide, halosulfuron-methyl was studied in seven Japanese soils with different physicochemical properties. Soils were equilibrated with four levels of concentrations of halosulfuron-methyl using batch technique. Sorption affinity for halosulfuron-methyl was approximated by the Freundlich constant ( $K_f$ ), distribution coefficient ( $K_d$ ), and the normalized  $K_d$  based on organic carbon content ( $K_{oc}$ ). The sorption isotherms followed the Freundlich equation. Freundlich  $K$  values indicated that organic carbon was the predominant factor for halosulfuron-methyl sorption in the soils. Sorption was highly correlated with soil organic content and inversely correlated with soil pH. However, there was no significant correlation with clay content and cation exchange capacity of the soils.

## INTRODUCTION

Various soil properties have been shown to influence the retention and mobility of pesticide in the soil profile, including soil texture, soil organic matter, cation exchange capacity (CEC), soil acidity, Fe and Al oxide content, clay content and mineralogy. Studies on the relationships between selected soil properties and herbicide sorption can be useful in determining the amount of the chemical available for losses due to volatilization, leaching, and chemical and biological degradation.<sup>1,2)</sup>

Halosulfuron methyl [NC-319, methyl 3-chloro-5-(4,6-dimethoxypyrimidin-2-ylcarbamoylsulfamoyl)-1-methylpyrazole-4-carboxylate] is a novel sulfonylurea herbicide developed by Nissan Chemical Industries, Ltd., with its extremely high activities against various broad-leaf weeds.<sup>3)</sup>

Information on the behavior of halosulfuron-methyl in soil is essential in predicting its leaching potential and contaminatin of groundwater. The objectives of the present study were to (a) determine the relationships between the soil propreties and the amount of halosulfuron-methyl sorption on soils, (b) describe the sorption by Freundlich equation, and (c) correlate the Freundlich constant ( $K_f$ ) and distribution coefficient ( $K_d$ ) of halosulfuron-methyl in the soils with various soil

characteristics. The seven Japanese soils used were selected based on their wide range in particle size distribution, CEC, pH and organic carbon content.

## MATERIALS AND METHODS

### 1. Chemical

Analytical grade of halosulfuron-methyl (99.8% purity) as used in previous study<sup>4)</sup> was supplied by Nissan Chemical Industries, Ltd.

### 2. Soils

Seven Japanese soils differing widely in their physicochemical properties (Table 1) were used in the study. Soil samples were air-dried, ground and passed through a 2-mm sieve. Analysis to characterize the soils included determination of pH, CEC, organic carbon, and particle size distribution. Soil pH was measured in a soil/water (1:2.5, w/w) mixture with a glass electrode pH meter. The CEC was obtained by summation of exchangeable Na, K, Mg, and H.<sup>5)</sup> Organic carbon was estimated by the Walkey and Black method and organic matter (OM) was calculated by multiplying the values of organic carbon with 1.72.<sup>6)</sup> The soils were analyzed for clay, silt, and sand by the Bouyoucos hydrometer method.<sup>5)</sup>

### 3. Sorption and Desorption Procedures

#### 3.1 Sorption study

A stock solution of halosulfuron-methyl (3 mg l<sup>-1</sup>)

\* Studies on the fate and behavior of the herbicide halosulfuron-methyl in the soils (Part 2).

was prepared in 0.01 M  $\text{CaCl}_2$ . The four concentrations used in the equilibration (0.3, 0.5, 1.0 and 3.0  $\text{mg l}^{-1}$ ) of halosulfuron-methyl were prepared by dilution with 0.01 M  $\text{CaCl}_2$ . The 0.01 M  $\text{CaCl}_2$  background electrolyte was used to mimic electrolyte concentrations in natural solutions found in many soils and to enhance separation of solid materials from aqueous solution after equilibration. A 10 ml aliquot of each of the four halosulfuron-methyl solutions and a control solution (0  $\text{mg l}^{-1}$ ) was added to 2 g of air-dried soil in a 25 ml centrifuge tube, and the tube was sealed with a parafilm and foil-lined cap. For Saitama-2 soil containing high organic matter, a 1 g of air-dried soil was used because of its high capability to sorb the chemical. The tubes were placed on a water-bath shaker and shaken for 24 h at 20°C. The 24 h time period was determined previously to be adequate for short-term equilibrium; longer shaking times were avoided to minimize the potential for microbial degradation of the chemical. After shaking, the slurries were centrifuged at  $14,000 \times g$  for 20 min. A five ml aliquot of the supernatant was taken and filtered through MILLEX®-PF Particulate Filter Unit (Milipore, Bedford). The concentrations of halosulfuron-methyl were determined using HPLC by the same method reported previously for the degradation study.<sup>4)</sup> All sorption studies were conducted using duplicate soil samples for each initial concentration and for each of the seven soils. Soil-less tubes with only the initial solutions and chemical-less tubes with only soil and  $\text{CaCl}_2$  solution received the same handling and analysis, and were used as reference blanks and control.

The amount of halosulfuron-methyl sorbed to the soil after equilibration was the difference between halosulfuron-methyl concentration before and after equilibration as follows:

$$X = ((C_0 - C_1)V) / \text{soil mass}$$

where  $X$  is the mass sorbed in  $\text{mg kg}_{\text{soil}}^{-1}$ ,  $C_0$  = initial concentration in  $\text{mg l}^{-1}$ ,  $C_1$  = final concentration in  $\text{mg l}^{-1}$ ,  $V$  = volume of solution added in  $l$ , and soil mass is on an air-dried basis in  $\text{kg}$ .

### 3.2 Desorption study

Desorption was determined by using the same samples with the initial concentration of 1  $\text{mg l}^{-1}$  and 3  $\text{mg l}^{-1}$  that had been used for sorption studies. All of the supernatant was removed from each tube and replaced with fresh 0.01 M  $\text{CaCl}_2$ , then the tubes were shaken again for 24 hr, followed by centrifugation. The residual was again shaken with fresh 0.01 M  $\text{CaCl}_2$  and centrifuged, and the procedure was repeated once more. The supernatant from each run was filtered through MILLEX®-PF, and 20  $\mu\text{l}$  of an aliquot was analyzed by HPLC.

## RESULTS AND DISCUSSION

### 1. Soil Properties

As shown in Table 1, clay contents ranged from 4.8 to 46.8%, soil pH values ranged from 4.8 to 6.6, organic carbon contents ranged from 0.38 to 6.74%, and CEC of the soils ranged from 2.1 to 22.2  $\text{meq } 100 \text{ g}^{-1}$ .

### 2. Sorption Isotherms

Sorption isotherms for halosulfuron-methyl were described quantitatively by Freundlich equation:

$$X = K_f C_i^{1/n}$$

where  $K_f$  is the Freundlich coefficient,  $1/n$  is the Freundlich exponent, and  $X$  and  $C_i$  are as defined above. Values of  $K_f$  and  $1/n$  were estimated by linear regression after log-log transformation. Halosulfuron-methyl sorbed by the soils after equilibration was plotted following the linearized form of the Freundlich equation (Fig. 1).

When the Freundlich isotherm slope is close to 1, the  $K_f$  values were approximated by  $K_d$  (distribution coefficient), the ratio of adsorbed halosulfuron-methyl to the concentration in the equilibrium solution. The variability of  $K_d$  with soil properties can be normalized by taking into account the organic carbon fraction:

$$K_{oc} = K_d / f_{oc}$$

where  $f_{oc}$  is the fraction (mass basis) of organic carbon in the soil. This relationship indicates that soil sorption is

Table 1 Selected properties of soils used for sorption isotherm experiments.

Site	Main clay <sup>a)</sup> mineral	Texture <sup>b)</sup>	Particle size distr.			CEC	Organic carbon	pH ( $\text{H}_2\text{O}$ )
			Sand	Silt	Clay			
Anjo	K	CL	33.1	28.5	38.4	9.5	1.24	6.46
Chiba		S	91.2	4.0	4.8	2.1	0.47	6.61
Ibaraki	A	HC	18.4	34.8	46.8	22.2	3.65	6.55
Nagano	M	SiCL	21.2	41.3	37.5	14.7	1.35	6.15
Saitama-1		SCL	65.8	18.6	15.5	10.5	0.76	5.37
Saitama-2		CL	30.3	39.3	30.4	18.3	6.74	4.82
Miyazaki		S	86.2	8.4	5.4	3.3	0.38	6.38

<sup>a)</sup> A : alophaine ; K : kaoline ; M : montmorillonite.

<sup>b)</sup> CL : clay loam ; HC : heavy clay ; S : sand ; SCL : sandy clay loam ; SiCL : silty clay loam.

linearly related to the amount of organic carbon in soil. Freundlich constant ( $K_f$ ) expressed the amount of halosulfuron-methyl sorbed and was highest for Saitama-2 soil which was highest in soil organic carbon content, and lowest for Miyazaki soil which was lowest in soil organic carbon content (Table 2). Sorption of

halosulfuron-methyl increased very significantly with increasing soil organic carbon content. The  $K_f$  value of halosulfuron-methyl on the seven soils ranged from 0.51 to 9.65 which implied that the halosulfuron-methyl sorption varied with soil type.  $K_f$  values of Anjo and Nagano soils (2.50 and 2.58, respectively) were comparable to  $K_f$  value for chlosulfuron (2.4) sorbed to Acredale silt loam soil of almost similar organic carbon content.<sup>7)</sup>

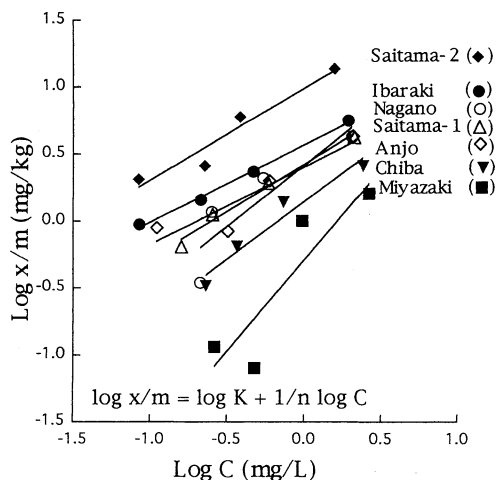


Fig. 1 Freundlich-Van Bemmelen adsorption isotherms for the adsorption of halosulfuron-methyl by seven Japanese soils (2 g soil : 10 ml 0.01 M CaCl<sub>2</sub>, 20°C, 24 hr).

Table 2 Halosulfuron-methyl adsorption parameter for Freundlich model and distribution coefficient ( $K_d$ ) values.

Site	$K_f$	Freundlich isotherm		$K_d$ <sup>b)</sup>	$K_{oc}$ <sup>a)</sup>
		1/n	r <sup>2</sup>		
Anjo	2.50	0.58	0.92	4.07	328
Chiba	1.39	0.86	0.97	1.55	329
Ibaraki	3.65	0.57	0.99	6.37	174
Nagano	2.58	0.91	0.89	3.06	226
Saitama-1	2.62	0.70	0.99	3.46	455
Saitama-2	9.65	0.68	0.97	15.29	227
Miyazaki	0.51	1.36	0.89	0.37	96
Mean	3.27	0.81	0.95	4.88	262

a)  $K_d$  normalized for organic carbon content.

b)  $K_d$  amount adsorbed ( $\mu\text{g/g}$ )/equilibrium concentration ( $\mu\text{g/ml}$ ) (mean values for concentrations of 0 to 3  $\mu\text{g/ml}$ ).

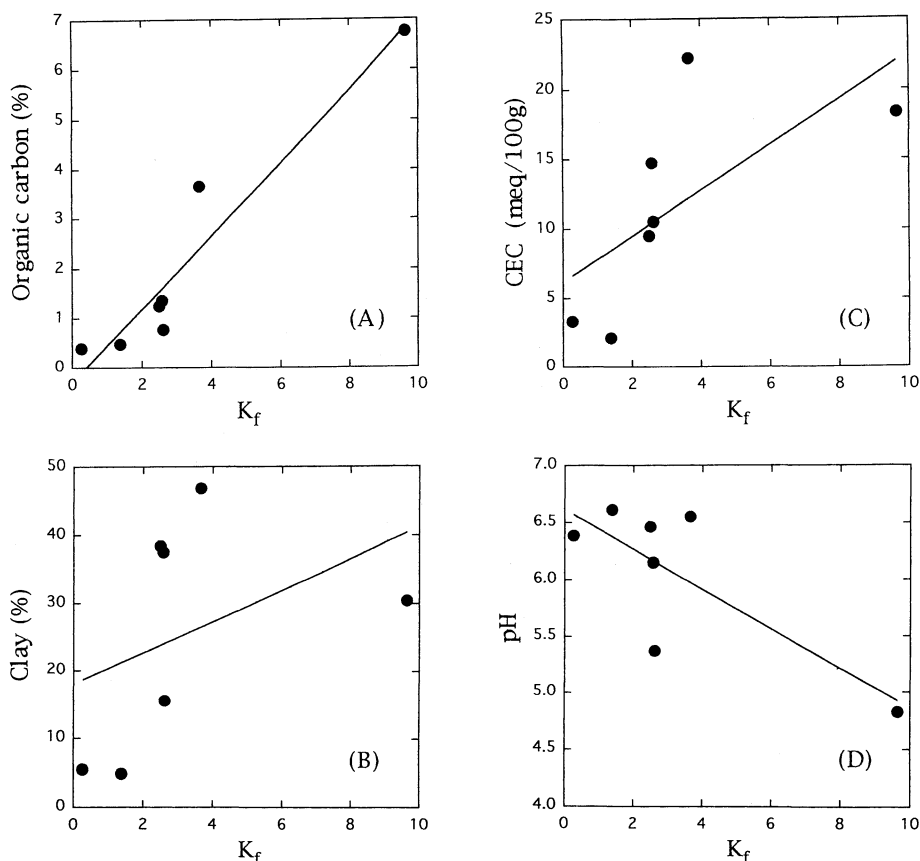


Fig. 2 Relationship of organic carbon content (A), clay content (B), CEC (C) and pH (D) of seven soils with halosulfuron-methyl  $K_f$  values (conditions same as Fig. 1).

Values of Freundlich parameter  $1/n$ , were less than 1.0 for all soils, except for Miyazaki soil. This is the results of decreased adsorption as the sorptive sites became occupied. Therefore, in this study, using the nonlinear isotherm is more appropriate for the remaining soils than the linear isotherm.

However, linear sorption isotherms are frequently used in transport models to account for retention of herbicides in soils. Therefore,  $K_d$  and  $K_{oc}$  values were also calculated for halosulfuron-methyl (Table 2). Trends in  $K_d$  were similar to those of  $K_f$ , as shown in Saitama-2 soil having the greatest affinity and in Miyazaki soil having the least affinity for halosulfuron-methyl.

Regression analysis between  $K_f$  values and clay contents, organic carbon contents, pH, and CEC of the soils were performed (Table 3, Fig. 2).  $K_f$  values were very highly correlated with organic carbon content ( $r=0.96$ ), and inversely correlated with soil pH ( $r=0.78$ ) but not correlated to CEC ( $r=0.67$ ). Low correlation coefficient ( $r=0.41$ ) was obtained when clay contents was correlated with  $K_f$  values. With chlorsulfuron, Mersie and Foy<sup>6</sup>) found that correlation coefficient between Freundlich  $K$  of chlorsulfuron for four soils and percent organic carbon resulted in  $r=0.87$ , and between  $K$  and percent clay resulted in  $r=0.09$ . These suggested that the sorption of sulfonylurea herbicides in soils was highly correlated with soil organic carbon and not correlated with soil clay contents. However, when multiple linear regression analysis was utilized using two soil parameters (% clay+other parameters) to describe halosulfuron-methyl sorption by the 7 soils, much higher correlation coefficient ( $r=0.76-0.97$ ) was resulted than regression analysis in which % clay content alone was used (Table 3).

$K_{oc}$  values did not appear to be related to organic matter contents of the soils (Table 2). Kozak and Weber<sup>8</sup>) also found similar results for adsorption studies on five phenylurea herbicides in 8 Czechoslovakian soils.

Table 3 Correlation coefficient ( $r$ ) of distribution coefficient ( $K_d$ ) and Freundlich constant ( $K_f$ ) for halosulfuron-methyl on seven soils with various soil parameters.

Soil parameter	Distribution coefficient ( $K_d$ )	Freundlich constant ( $K_f$ )
Organic Carbon (%)	0.975**	0.956**
Clay content (%)	0.444	0.413
Clay and silt content (%)	0.759	0.805*†
Clay and organic matter content	0.973**	0.958**†
pH	-0.731	-0.775*
CEC (meq/100 g)	0.687	0.666

\*,\*\* : Significant at the 0.05 and 0.01 levels, respectively.

†  $K_d$  and  $K_f$  using two soil parameters were calculated by multiple linear regression analysis,  $Y = a + b_1X_1 + b_2X_2$ .

According to them, either the organic matter in each of the soils was similar or other colloidal surfaces also contributed to herbicide sorption. Moreover, sorption was not correlated with the clay content of the soils indicating that organic coatings on clay in soils may block sorption sites on clay surfaces.

### 3. Desorption

Desorption pattern for halosulfuron-methyl in soils are illustrated in Fig. 3. By the end of three desorption cycle, the amount desorbed was 9.5, 0.0, 49, 19, 39, 24, and 0.0% for Anjo, Chiba, Ibaraki, Nagano, Saitama-1, Saitama-2, and Miyazaki soil, respectively. The desorption of halosulfuron-methyl was highest in Ibaraki soil which has highest CEC and clay content. This indicates that CEC and clay content are not the factors for retention of halosulfuron-methyl. On the other hand, halosulfuron-methyl was poorly desorbed from Saitama-2 soil which has the highest organic carbon content. This suggests that organic matter content tightly retained halosulfuron-methyl. Hence, desorption process of halosulfuron-methyl from soils was not affected by clay binding but strongly affected by organic binding.

However, in case of Chiba and Miyazaki sandy soils which have low organic matter content, the desorption seemed none in Fig. 3. On the basis of OECD guidelines, the desorption test of chemical is called for if the sorption is significant (*ca.* 25% or more).<sup>9</sup> The adsorption on these soils was very low (*ca.* 10%, not listed), and hence, the amount desorbed was within the technical limitation.

The relationship between degradation and sorption of halosulfuron-methyl in the soils was noticed. Halosulfuron-methyl degraded faster in Anjo soil than Nagano soil under various moisture contents at 25°C.<sup>4</sup> As mentioned before, the sorption of halosulfuron-methyl was higher in soils with higher organic matter

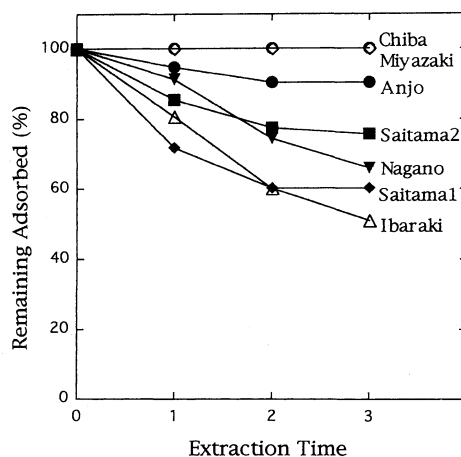


Fig. 3 Desorption of halosulfuron-methyl (3 ppmw) from seven Japanese soils expressed as percentage of remaining adsorbed after each successive extraction.

content or lower pH. Therefore, higher organic carbon content and lower pH Nagano soil resulted in stronger halosulfuron-methyl sorption in Nagano soil than Anjo soil. Slower degradation in Nagano soil seemed to correlate to higher sorption of halosulfuron-methyl in the Nagano soil; *vice versa* for Anjo soil.

In summary, the magnitude of halosulfuron-methyl sorption in this study was described equally well by both the nonlinear Freundlich models and linear  $K_d$ , although the nonlinear model was probably more appropriate. There was a correlation between sorption and organic carbon, and pH, but there was no strong relationship with clay and CEC. These results imply that halosulfuron-methyl applied to soils with higher organic matter and low pH are strongly sorbed and weakly desorbed and hence will not cause water pollution.

#### ACKNOWLEDGMENTS

We wish to thank Dr. H. Honda and Dr. T. Miyamoto of our laboratory for their invaluable suggestions and also to Dr. H. Igarashi of Nissan Chemical Industries, Ltd., for supplying authentic chemicals and some of the soils. We also acknowledge Dr. K. Nakamura of Saitama Agricultural Experimental Station for supplying Saitama-2 soil and also Dr. M. Kimura and Dr. A. Katayama of Nagoya University for supplying Anjo and Nagano soils.

#### REFERENCES

- 1) C. A. I. Goring, D. A. Laskowski, J. W. Hamaker & R. W. Meikle: "Environmental Dynamics of Pesticides," ed. by R.

Haque & V. H. Freed, Plenum Press, New York, pp. 135-172, 1975

- 2) R. Haque: "Environmental Dynamics of Pesticides," ed. by R. Haque & V. H. Freed, Plenum Press, New York, pp. 97-114, 1975
- 3) T. Nawamaki, T. Sato, S. Yamamoto & K. Suzuki: Abstr.: 21th Pestic. Sci. Soc. Jpn., p. 83, 1996 (in Japanese)
- 4) Dermiyati, S. Kuwatsuka & I. Yamamoto: *J. Pesticide Sci.* **22**, 282-287
- 5) C. A. Black: "Methods of Soil Analysis," Part 2, American Society of Agronomy, Madison, Wisconsin, 1965
- 6) M. L. Jackson: "Soil Chemical Analysis," Prentice-Hall of India, 1967
- 7) W. Mersie & C. L. Foy: *J. Agric. Food. Chem.* **34**, 89 (1986)
- 8) J. Kozak & J. B. Weber: *Weed Sci.* **31**, 368 (1983)
- 9) OECD: "Guidelines for Testing of Chemicals," Part II (106), OECD, Paris, 1981

#### 要 約

#### 日本土壌における除草剤ハロスルフロロンメチルの土壌特性と土壌吸着との関連性

Dermiyati, 鎌塚昭三, 山本 出  
スルホニル尿素除草剤のハロスルフロロンメチル (NC-319) についての土壌吸着を、物理化学的性質の異なる7種類の土壌を用いて研究した。4段階の濃度でバッチ法で研究した。吸着等温線は Freundlich 式に従った。Freundlich-K 値から有機炭素が吸着の主要因子であることを示した。吸着は土壌有機物量と高い正の相関を示し、土壌 pH と負の相関を示した。粘土含量とカチオン交換容量は吸着との間に有意の相関を示さなかった。