(75)　　　　３つの土壌への 2,4-D（2,4-ジクロロフェノキシ酢酸）の吸着における pH の影響

The Effect of pH on Sorption of 2,4-D on Three Soils

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ABSTRACT　The effect of pH on the sorption of the herbicide 2,4-D (2,4-dichlorophenoxyacetic acid) on one tropical soil (Dark Red Latosol) and two Japanese soils (Brown Forest Soil and Granitic Regosol) has been studied with a batch equilibration technique. In the range of relatively low concentrations of 2,4-D (0.5-50 mg.L^{-1}), linear isotherms were obtained to give the sorption coefficient K_d of 0.016-2.76 L.kg^{-1} at pH 3.4-7.9. The sorption of 2,4-D on three soils, as measured by K_d, increased with decreasing pH of the solution of 2,4-D. The effect of concentration of hydrogen ion (H$^+$) on K_d was summarized as $K_d = k[H^+]^m$, where k is a constant and m is 0.33-0.42. The effects of organic matter content, CEC and clay contents of the soils were also studied. The 2,4-D concentration in aqueous phase was determined using HPLC-UV system.

KEYWORDS : 2,4-D, soil, adsorption coefficient, pH, HPLC

1. Introduction

Soil is known to function as a chemical as well as a biological filter, which lessens the environmental impact of organic chemicals introduced into the biosphere by many processes. Soils acts as a first line of defense against the leakage of these compounds into the groundwater, by adsorbing organic chemicals as well as biological and/or chemical degradation. Consequently, to predict the behavior of organic pollutants in soils and surface water, and to evaluate the risk for leaking a particular chemical into groundwater, it is necessary to understand the nature and extend of the sorption and the degradation [1]. The behavior of the pesticides residues in soils and surface water mainly depends on the sorption properties of the soil [2,3,4,5]. The herbicide 2,4-D is among the most widely used weed control agents and one of the most mobile pesticides for its low affinity to soil. 2,4-D is used in agriculture, home lawns, forestry, and road and railroad maintenance programs.

The purpose of this work is to examine the effect of pH on the sorption of 2,4-D on three different soils, i.e., an oxisol (Dark Red Latosol), a sandy loam soil (Granitic Regosol, truncated immature) and Brown Forest Soil, to compare relative sorption of 2,4-D on three soils and to discuss the sorption mechanism of 2,4-D onto soils.

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**広島大学大学院工学研究科物質化学システム専攻応用化学講座 (Graduate School of Engineering, Department of Chemistry and Chemical Engineering, Hiroshima University)
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2. Materials and Methods

2.1. Chemical

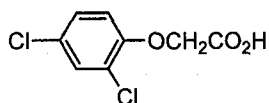Analytical grade 2,4-D ($\geq$ 98% purity) was obtained from Cica-Reagent (Fig.1).

Figure 1. Chemical structure of 2,4-D.

All other materials used were analytical reagent grade. Selected properties for 2,4-D are listed in Table 1.

Table 1. Selected chemical properties for 2,4-D.

Compound	Solubility in water (mg.L^{-1})	log K_{ow}[a]	pK_a	Mol. weight	Half life time in soil (days)	Vapor pressure at.25°C (mPa)
2,4-D	620	2.83	2.6	221	< 7	1.86×10^{-2}

[a] K_{ow} : Octanol/water partition coefficient

2.2. Soils

Three surface soils, Brown Forest Soil (BFS) collected at an agricultural site in the Zentsuji city, Kagawa pref., Granitic Regosol (GR) taken from the agricultural research field of Hiroshima University, and Dark Red Latosol collected from Faculty of Agricultural Science, São Paulo State University (UNESP), Botucatu city, São Paulo State, Brazil, were used in this experiment. The samples were air-dried overnight, sieved to < 2.0-mm mesh and stored in sealed containers at room temperature. Soil properties are shown in Table 2.

Table 2. Selected characteristics of the 3 soils.

Soil	Clay (%) (<2 μm)	Silt (%) (2 μm-50 μm)	Sand (%) (2mm-50 μm)	OM[a] (%)	CEC[b] (meq. 100g^{-1})	pH in water 1 : 2.5
Brown Forest	12.4	34.8	52.8	3.3	9.5	7.1
Dark Red Latosol	16	4.0	80.0	1.4	5.4	4.6
Granitic Regosol	9.0	19.8	71.2	1.1	3.4	5.85

[a] Organic matter
[b] Cation exchange capacity

2.3. Batch sorption measurement

The measurement of sorption isotherms was carried out with 4 initial concentrations (C_i) of 2,4-D from 0.5 to 50 mg.L^{-1} in 0.005 M CaSO$_4$ solution. The final pH of the solution was adjusted between 3.4 and 7.9 by adding dilute HCl or NH$_4$OH solutions. A 10 mL aliquot of each solution was added to 10g of soil (BFS, GR) in a 100 ml conical flask covered with aluminium foil, and was shaken on a wrist action shaker for 48 h, 50-60 rpm, at 25$\pm$1°C. For Latosol, was weighed 5 g of the soil and filled with 5 mL 2,4-D aqueous solution of each concentration. A preliminary kinetic study showed that 30 h was enough to reach sorption equilibrium and that the degradation of the herbicide scarcely occurred during this period. The suspensions were centrifuged for 10 min at 12,000 rpm, and the supernatant filtered through a 0.2 μm membrane filter (ADVANTEC). The amount of 2,4-D in supernatant was determined by HPLC analysis. All samples were run in duplicate and blank samples of soil were used.

2.4. Analytical method

The determination of the equilibrium concentration (C_e) of 2,4-D was performed using HPLC (SHIMADZU LC-10A) under the following conditions : Inertsil ODS-80A packed column (4.6x150mm); the

eluting solvent was made of equivolume of acetonitrile and water (containing 0.04% phosphoric acid); flow rate 1.0 mL/min; wavelength UV-225 nm and injection volume 20μl. The retention time of 2,4-D under these conditions was approximately 6.0 ± 0.5 min; and the detection limit was 0.25 $\mu g.ml^{-1}$. The analytical precision was $\pm 3.38\%$ based on standard samples.

2.5 Determination of sorption coefficient K_d

Sorption can be defined by two distinct approaches : the partitioning theory and the sorption-site theory. The former corresponds to the partitioning of a chemical between solid and liquid phases. At environmental concentrations (low concentrations), the sorption isotherm of organic pollutants in soil is frequently considered as linear, meaning that the sorbed pollutant concentration is linearly related to the liquid pollutant concentration. In this case, sorption isotherms can be represented by

$$C_s = K_d C_e \qquad (1)$$

where C_s is the amount of adsorbed chemicals (mg.kg^{-1}), C_e is the equilibrium concentration (mg.L^{-1}) of solution phase, and K_d is a sorption coefficient or distribution coefficient (L.kg^{-1}).

3. Results and Discussion

3.1. Time course of 2,4-D sorption

Preliminary batch experiments were done to measure the time course of 2,4-D sorption. A solution of 2,4-D (50 mg.L^{-1}) was added to the weighed soils and the concentrations of the herbicide (C_w) were measured after 0.17, 0.5, 1.0, 4.0, 8.0, 24 and 48 hours of shaking. The time courses of decrease of 2,4-D in the solution were demonstrated in Fig.2. For three soils, an apparent sorption equilibrium has been reached after 24 h and the equilibrium concentration (C_e) was obtained.
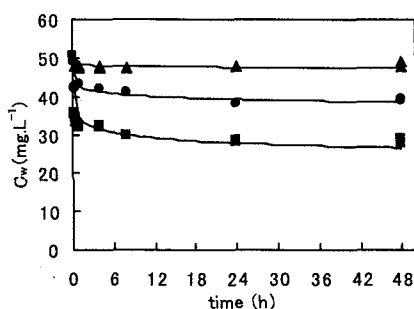

Figure 2. Time course for 2,4-D sorption on Granitic Regosol (triangle), Brown Forest Soil (circle) and Dark Red Latosol (square) at natural soil pH.
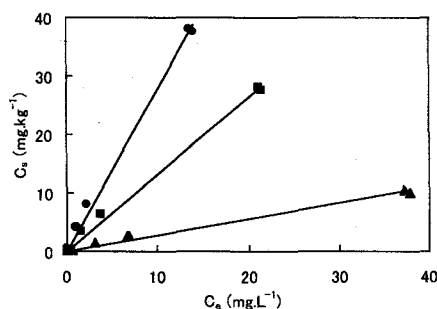
Figure 3. Typical linear isotherm of 2,4-D sorption on Brown Forest Soil (circle), Dark Red Latosol (square) and Granitic Regosol (triangle) at acid pH 4.2, 3.4 and 4.1 respectively.

3.2. Determination of sorption coefficient (K_d)

For each batch equilibration experiments of 2,4-D, the amount of 2,4-D adsorbed (C_s) was calculated according to the following equation :

$$C_s = V(C_i . C_e)/ M \qquad (2)$$

where C_s is the adsorbed fraction of herbicide in mg.kg^{-1} of soil, C_i and C_e are the initial and equilibrium concentrations in mg.L^{-1}, respectively, V is the total volume of solution in liters, and M is the mass of soil material in kilograms. The plots of C_s against C_e gave linear relationship in the range of 2,4-D concentration of

0.5-50 mg.L^{-1}, as illustrated in Fig.3. The correlation factor (r^2) was more than 0.9 as summarized in Table 3. The slope of the straight line in Fig.3 directly gives the sorption coefficient K_d (L.kg^{-1}) according to Eq.1.

Frequently a Freundlich type of isotherms has been reported for the sorption of 2,4-D. In these cases, a relatively high concentration of 2,4-D (20-200 mg.L^{-1}) was applied, whereas the concentration of 2,4-D in the present work was low (0.5-50 mg.L^{-1}) .

As described in the introduction section, the information of the herbicide behavior in low concentration should be required to predict the behavior of organic pollutants in soils and surface water, and to evaluate the risk for leaking a particular chemical into groundwater.

3.3. Effect of pH on herbicide sorption

The Table 3 summarizes the sorption parameters obtained by batch experiments for three soils in different pH of 2,4-D solutions. For three soils tested, the sorption coefficient increased with decreasing pH.

Table 3. Sorption coefficient of 2,4-D on three soils at various pH.

| Soil	pH	K_d (L.kg^{-1})	r^2
Brown Forest Soil	4.2	2.761	0.993
	6.1	0.386	0.976
	6.9	0.232	0.965
	7.9	0.075	0.872
Dark Red Latosol	3.4	1.319	0.991
	4.3	0.828	0.988
	7.1	0.057	0.996
	7.6	0.025	0.925
Granitic Regosol	4.1	0.278	0.979
	6.3	0.032	0.823
	7.1	0.028	0.970
	7.8	0.016	0.970

Previous studies of 2,4-D sorption on oxisols at different depths by Barriuso et al. [6] and on silt loams by Baskaran et al. [7] also showed that sorption coefficient increased with decreasing pH. Acidic organic chemicals such as 2,4-D and 2,4-DP (2,4-dichlorophenoxypropionic acid) exist as either the neutral form (HA) or the anion form (A$^-$) according to the dissociation equilibrium shown in the scheme 1. An increase of the pH of the system will favor the formation of ionized species (A$^-$). One can calculate the relative concentrations of the neutral and ionic species using the value of pKa (Table 1), which is the logarithm of the dissociation constant of 2,4-D. The Table 4 summarizes the result of the calculated concentrations of HA and A$^-$. As seen in Table 4, the concentration of the ionic species is essentially constant between pH 4 and 8, while the neutral one increases with decreasing pH, suggesting that the neutral form of 2,4-D predominantly adsorbs on the soil.

The logarithmic plot of K_d against pH gave a linear relationship as seen in Fig. 4.
According to the linear relationship, one can formulate the effect of pH on K_d as Eq. 3.

$$K_d = k \times [H^+]^m \tag{3}$$

where k is a constant for a given soil.

The experimental values of m were 0.33-0.42 for three soils. The results reported by Barriuso et al. [6] are also plotted in Fig. 4. In agreement with the present work, the plots of logarithm of K_d against pH gave linear relationship with slopes of 0.27-0.42 (Table 4). If the effect of pH on K_d as demonstrated in Fig. 4 is solely caused by the change in the concentration of neutral species (HA) of the herbicide, the values of m observed should be unity. One might argue that the chemical properties of the soil also change with pH variation and the thus the m values for the sorption of 2,4-D on the soil will deviate from unity. The effect of pH on the chemical properties of the soil surface can be estimated from the sorption experiments for the effect of pH on K_d of a neutral herbicide, atrazine [6,7]. The sorption coefficients of atrazine on various soils are essentially independent of pH of the solutions, suggesting that the change in chemical properties of the soil surface would not affect the sorption coefficient of neutral herbicides such as atrazine and the neutral form (HA) of 2,4-D.
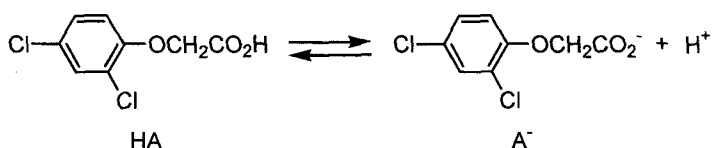
Scheme 1. Neutral (HA) and ionic (A⁻) forms of 2,4-D.

Table 4. Calculated concentration of the neutral (HA) and ionic (A⁻) species of 2,4-D at pH 4-8.

pH	$[HA]/[HA]_0$	$[A^-]/[HA]_0$
4	3.829×10^{-2}	0.9617
5	3.965×10^{-3}	0.9960
6	3.979×10^{-4}	0.9996
7	3.981×10^{-5}	1.0000
8	3.981×10^{-6}	1.0000

$[HA]_0$ = total concentration of 2,4-D = $[HA] + [A^-]$
$[HA]$ = concentration of neutral form of 2,4-D
$[A^-]$ = concentration of ionic form of 2,4-D

3.4. Effect of soil type on sorption

The effect of soils on the sorption of 2,4-D is in Fig. 4. The Brown Forest Soil adsorbed much more than Granitic Regosol and Dark Red Latosol in all pH range.
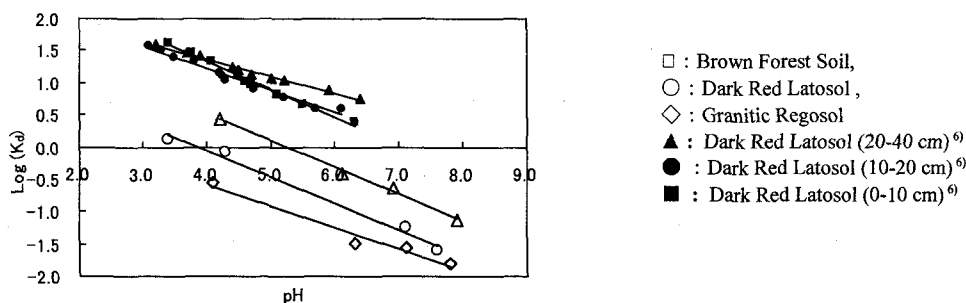

□ : Brown Forest Soil,
○ : Dark Red Latosol ,
◇ : Granitic Regosol
▲ : Dark Red Latosol (20-40 cm)[6]
● : Dark Red Latosol (10-20 cm)[6]
■ : Dark Red Latosol (0-10 cm)[6]

Figure 4. The relationship between log (k_d) and pH of the soils.

Table 5. The parameters graphically obtained from Fig.4 and Eq.3

Soil	m	r^2
Granitic Regosol	0.33	0.965
Dark Red Latosol	0.41	0.988
Brown Forest Soil	0.42	0.995
Dark Red Latosol (0-10 cm)[6]	0.42	0.993
Dark Red Latosol (10-20 cm)[6]	0.31	0.969
Dark Red Latosol (20-40 cm)[6]	0.27	0.994

It is well known that anionic compounds are poorly adsorbed on clay minerals but could be moderately retained by positively charged organic matter [9,10,11,12]. In agreement with the reported effect of organic matter by Barriuso et al.[6], the value of K_d increases with increasing the organic matter content, as shown in Fig.5a.

The K_d also depends on CEC (cation exchange capacity), as shown in Fig.5b, while no correlation was observed between K_d and the clay content as seen in Fig.5c. The correlation found in Figs. 5a and 5b is, however, seems to be an apparent one, because the K_d in Figs. 5a and 5b are for different soils with different mineral contents.
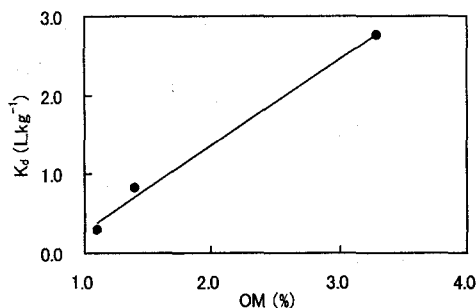

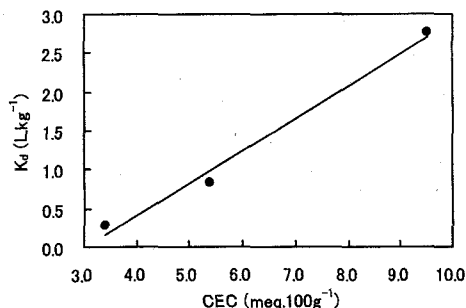**Figure 5a.** Relation between OM and K_d for three soils at pH 4.1-4.3.

Figure 5b. Relation between CEC and K_d for three soils at pH 4.1-4.3.
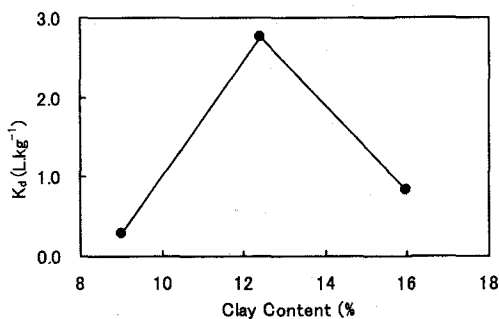

Figure 5c. Plot of Clay Content against K_d of three soils at pH 4.1- 4.3.

4. Conclusions

The results of these sorption experiments of 2,4-D lead to the following conclusions :

1. For three soils, the effect of pH on K_d is significant.
2. K_d also depends on the content of organic matter and CEC.
3. No correlation is observed between K_d and the clay content.

5. References

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