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Adsorption of 2,4-Dichlorophenoxyacetic Acid onto Volcanic Ash Soils: Effects of pH and Soil Organic Matter

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Abstract

The quantification of the linear adsorption coefficient (K_d) for soils plays a vital role to predict fate and transport of pesticides in the soil-water environment. In this study, we measured K_d values for 2,4-Dichlorophenoxyacetic acid (2,4-D) adsorption onto Japanese volcanic ash soils with different amount of soil organic matter (SOM) in batch experiments under different pH conditions. All measurements followed well both linear and Freundlich adsorption isotherms. Strong correlations were found between measured K_d values and pH as well as SOM. The 2,4-D adsorption increased with decreasing pH and with increasing SOM. Based on the data, a predictive K_d equation for volcanic ash soils, log (K_d) = 2.04 - 0.37 pH + 0.91 log (SOM), was obtained by the multiple regression analysis. The predictive K_d equation was tested against measured 2,4-D sorption data for other volcanic ash soils and normal mineral soils from literature. The proposed K_d equation well predicted K_d values for other volcanic ash soils and slightly over- or under-predicted K_d values for normal mineral soils. The proposed K_d equation performed well against volcanic ash soils from different sites and countries, and is therefore recommended for predicting K_d values at different pH and SOM conditions for volcanic ash soils when calculating and predicting 2,4-D mobility and fate in soil and groundwater.

Keywords: 2,4-D; adsorption; volcanic ash soil; pH; SOM

1. Introduction

Adsorption is a key process governing fate and transport of pesticides in soil-water environment. The adsorption studies can provide the essential information for predicting and estimating availabilities of pesticides for degradation, transformation and uptake by organisms, leaching through the soil profile, and retention in the soils (Bailey and White, 1970; Hornsby *et al*., 1996). The distribution of pesticides between soil and aqueous phases can be expressed in term of linear adsorption coefficient, K_d (Spark, 2003; Essington, 2004).

Among widely used pesticides, 2,4-dichlorophenoxyacetic acid (2,4-D) is an oldest and well known herbicide because of its good selectivity and inexpensive cost (Tu *et al*., 2001). Therefore, many researches of 2,4-D adsorption onto soils have been conducted (e.g., Barriuso and Calvet, 1992; Boivin *et al*., 2005; Calvet *et al*., 2007). Despite much work being carried out on 2,4-D adsorption onto soils, very few studies have recently focused on volcanic ash soils (eg., Hiradate *et al*., 2007; Müller and Duwig, 2007). Especially, quantitative descriptions of K_d as functions of impact factors on adsorption such as pH and soil organic matter (SOM) for volcanic ash soils are very limited.

The purposes of this study were i) to measure adsorption coefficients, K_d, of 2,4-D onto Japanese volcanic ash soils with different SOM at different pH, ii) to examine the effects of pH and SOM on K_d values, and iii) to propose a predictive K_d equation and test against the measured 2,4-D adsorption data for other volcanic ash soils and normal mineral soils from different sites and countries.

2. Materials and Methods

2.1. Volcanic ash soils

Volcanic ash soils (Androsols) are distributed across around 0.84% of the earth's land surface

Table 1. Selected characteristics and measured adsorption coefficients for volcanic ash soils.

No.	Soils	pH	SOM(%)	CEC (meq/100g)	Sand(%)	Silt and Clay(%)	Linear isotherm		Freundlich isotherm		
							K_d	r^2	K_f	n	r^2
1	Fukushima (10-15cm, Forested)	4.3	7.9	na†	64.7	35.3	41.1	0.97	52.5	1.1	0.95
2		5.7*	7.9	41.3	64.7	35.3	12.5	0.96	17.1	1.0	0.93
3		6.9	7.9	na†	64.7	35.3	4.7	0.96	6.5	1.0	0.96
4		7.8	7.9	na†	64.7	35.3	3.7	0.93	5.5	1.0	0.95
5	Fukushima (15-20cm, Forested)	4.2	3.3	na†	68.9	31.1	9.7	0.99	10.4	1.0	0.99
6		5.7*	3.3	23.5	68.9	31.1	2.5	0.99	3.0	1.0	0.99
7		7.0	3.3	na†	68.9	31.1	0.8	0.99	1.1	0.9	0.99
8		7.9	3.3	na†	68.9	31.1	0.4	0.99	0.6	0.9	0.99
9	Fukushima (20-25cm, Forested)	4.2	1.7	na†	53.9	46.1	5.7	0.99	6.5	1.0	0.99
10		5.7*	1.7	na†	53.9	46.1	1.3	0.99	2.0	0.9	0.99
11		6.9	1.7	na†	53.9	46.1	0.3	0.95	0.8	0.8	0.98
12		7.9	1.7	na†	53.9	46.1	0.2	0.99	0.4	0.8	0.99
13	Nishi-Tokyo (0-15cm, Cultivated)	4.7	9.2	na†	51.5	48.5	6.7	0.98	7.8	0.8	0.99
14		6.3*	9.2	42.8	51.5	48.5	2.4	0.99	2.1	1.1	0.99
15		6.7	9.2	na†	51.5	48.5	2.8	0.98	2.9	0.8	0.76
16		7.3	9.2	na†	51.5	48.5	0.5	0.99	0.9	0.7	0.99
17		8.4	9.2	na†	51.5	48.5	0.3	0.97	0.1	1.5	0.99
18	Nishi-Tokyo (0-10cm, Pasture)	4.0	19.3	na†	41.9	58.1	33.0	0.99	36.6	1.1	0.95
19		5.0	19.3	na†	41.9	58.1	15.1	0.99	15.3	0.8	0.99
20		6.8*	19.3	na†	41.9	58.1	8.3	0.99	9.2	0.8	0.99

* : natural pH
† : not avaliable

(Leamy, 1984) and 40% of national land in Japan is covered by the volcanic ash soils (JGS, 1974). The volcanic ash soils possess pH-dependent charges and are generally rich in minerals such as kaolinite, gibbsite, hematite and allophones (Shoji, 1986). In this study, volcanic ash soils were taken from two different sites in Japan: a hilly-forested site at Fukushima, and Tama Headquarters with Experimental Farm, Field Production Science Center, The University of Tokyo (TU FPSC) at Nishi-Tokyo. At Nishi-Tokyo site, soil samples were taken from both cultivated and pasture lands. Fukushima soil was taken from three different depths: 10-15, 15-20, and 20-25 cm. Nishi-Tokyo soil was collected from a depth of 0-15 cm at the cultivated land and from a depth of 0-10 cm at the pasture land. All soil samples were air-dried and sieved to obtain <2.0 mm.The selected physical and chemical properties for our volcanic ash soils are given in Table 1.

In this study, measured K_d values for other volcanic ash soils and normal mineral soils at different sites and countries from literatures were used to test a newly derived prediction equation for K_d. The measured K_d values for other volcanic ash soils are obtained from Hiradate *et al*. (2007) and Müller and Duwig (2007). In the former study, a volcanic ash soil was taken from Ap horizon at an upland experimental field of the National Institute for Agro-Environmental Sciences, Tsukuba, Japan. In the latter study, volcanic ash soils were taken from Mexico and New Zealand. The measure K_d values for normal mineral soils are obtained from Bekbölet *et al*. (1999) and Nishiguchi *et al*. (2003). In the former study, normal mineral sandy soils were taken from natural field sites in Turkey. In the latter study, mineral soils were collected from two cultivated lands and a forested land in Japan and Brazil (see Table 4).

2.2. 2,4-dichlorophenoxyacetic acid (2,4-D)

Analytical grade 2,4-dichlorophenoxy acid (2,4-D) ($\geq$ 98 % purity) was purchased from Wako Pure Chemical Industries, Ltd, Japan. It was used without further purification. The herbicide 2,4-D dissociates as a weak acid in an aqueous solution, with a predominant anionic form (Fig. 1). It is widely used for controlling broadleaf weeds on many crops, lawns and woody plants (Ghassemi *et al*., 1981; Howard, 1991). The selected chemical properties of 2,4-D are described in Table 2.

2.3. Batch adsorption method

Background solution of 2,4-D at different concentrations of 0-50 mg/L was prepared in 0.005M $CaSO_4$ or a mixed solution (0.085 mM NaCl + 0.015 mM $CaCl_2$). The 2,4-D solution was made in the solution with cations (eg., calcium, Ca; sodium, Na) in order to avoid changing the ionic strength of the soils when it was added to the soils, i.e., to avoid changing the chemical characteristics and structure of the soil

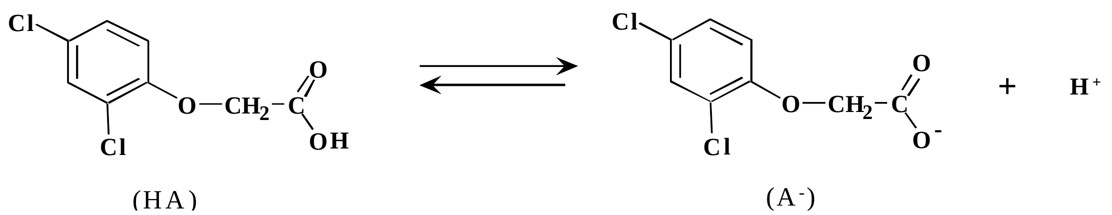


Figure 1. Neutral (HA) and ionic (A^-) forms of 2,4-D.

particles (Clay *et al.*, 1988; Farcasanu *et al.*, 1999). The 2,4-D solution was adjusted to obtain different pH by adding 0.1M HCl or 0.1 M NaOH (or 1.0 M NH_4OH).

The 10 ml of the prepared 2,4-D solution was added to 5g of air-dried soil sample in a conical flask. The conical flasks were shaken mechanically using a top table shaker for 24 or 48 hours at 25 ^oC. Here, the shaking time of 24 or 48 hours was determined based on the results obtained from another experiment that measured adsorption kinetics at different shaking times of 3, 6, 12, 18, 24, and 48 hours. After the shaking, the suspended solution was centrifuged for 30 min at 12000 rpm, and around 7 mL of supernatant was removed and filtered through a 0.22 μm glass fiber filter (Whatman GSWP, Whatman Ltd., England, UK). In order to measure the equilibrium concentration of 2,4-D solution, the filtered solution was analyzed by a high performance liquid chromatography (HPLC) (LC-6A, Shimazu, Kyoto, Japan) equipped with an UV-vis detector at 225 nm wavelength (SPD-10A, Shimazu, Kyoto, Japan), using a column (Luna 5uC18, Phenomenex, Torrance, CA, USA), and a delivering pump at constant flow rate of 1 mL/min and with a 20 μL injection volume. In the HPLC analysis, a mixed solution of ethanol (50%) and 0.04% H_3PO_4 solution (50%) was used as a carrier solution, and the retention time of the 2,4-D was approximately 7 min.

Measured data from the batch adsorption experiments were fitted with the linear adsorption isotherm equation [Eq. (1)] and the non-linear Freundlich isotherm equation [Eq. (2)].

The linear adsorption isotherm equation is:

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

where K_d is the linear adsorption coefficient (L/kg), S is the adsorbed amount of 2,4-D per unit mass of soil (mg/kg) (calculated from a mass balance equation) and C_e is the equilibrium concentration of 2,4-D in solution (mg/L). The Freundlich isotherm equation is:

$$S = K_f C_e^n \qquad (2)$$

where K_f is the Freundlich adsorption coefficient related to adsorption capacity, and n is the adsorption exponent related to adsorption intensity.

3. Results and Discussion

3.1. Adsorption coefficients of 2,4-D onto volcanic ash soils

A total of 20 measurements were carried out for Fukushima and Nishi-Tokyo volcanic ash soils with different amount of SOM at different pH in this study.

Table 2. Selected properties of 2,4-D. Data from Shiu *et al.*(1990), Tomlin (1994), and Hornsby *et al.*(1996).

Properties	**2,4-D**
Chemical Formula	$C_8H_6Cl_2O_6$
Chemical Family	Chlorinated phenoxy
Relative Molecular weight	221
Water Solubility	620-900 mg/L (25°C)
Octanol-water partition coefficient (K_{ow})	2.6-2.8 (pH1)
Dissociation constant (pK_a)	2.64-2.87

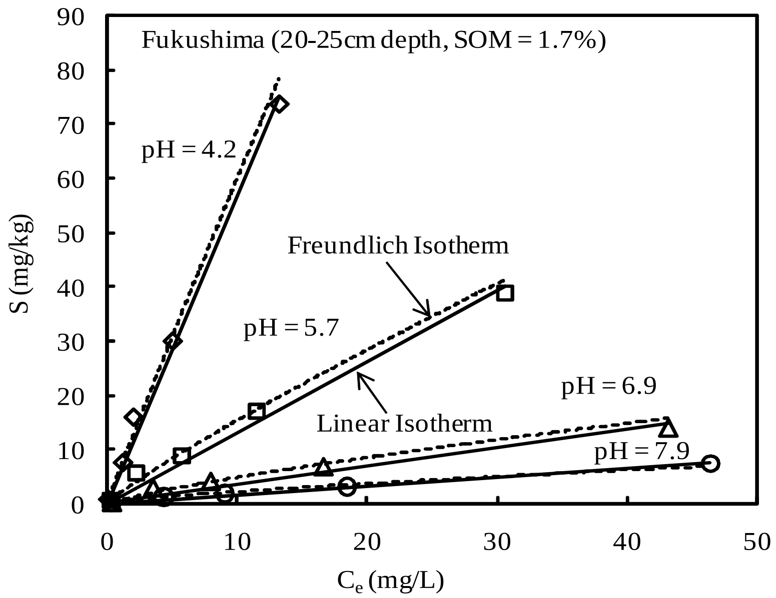


Figure 2. An example of linear and Freundlich adsorption isotherms for 2,4-D onto volcanic ash soil at different pH. Plots represent measured values. Solid lines show linear isotherms in Eq. (1) and dotted lines show Freundlich isotherms in Eq.(2).

An example of linear and Freundlich isotherms are depicted in Fig. 2. The measured K_d, K_f, and n values are reported in Table 1. All measurements in this study were well fitted with both linear and Freundlich adsorption isotherms. However, most of the measured n values in the Freundlich isotherms were approximately equal to 1, implying that the measured isotherms were likely to be linear.

In order to evaluate the effects of pH and SOM on adsorption of 2,4-D onto volcanic ash soils, the relationships between log-transformed K_d, log (K_d), and pH as well as log-transformed SOM, log (SOM), were depicted in Figs. 3(a-b). In Fig. 3(b), average of log (K_d) values in the four ranges of pH were plotted.

The log (K_d) clearly showed a negatively linear relationship with pH for each volcanic ash soil [Fig. 3(a)]. Several studies reported that the sorption of weakly acidic pesticides including 2,4-D depends on the pH and that the higher K_d values were observed at lower pH (Hermosin and Cornejo; 1991; Halfon *et al*., 1996; Carrizosa *et al*., 2000), while some studies gave an insignificant correlation between K_d values for 2,4-D sorption and pH (Boivin *et al*., 2005). For the range of pH investigated in this study (4.2-8.4),

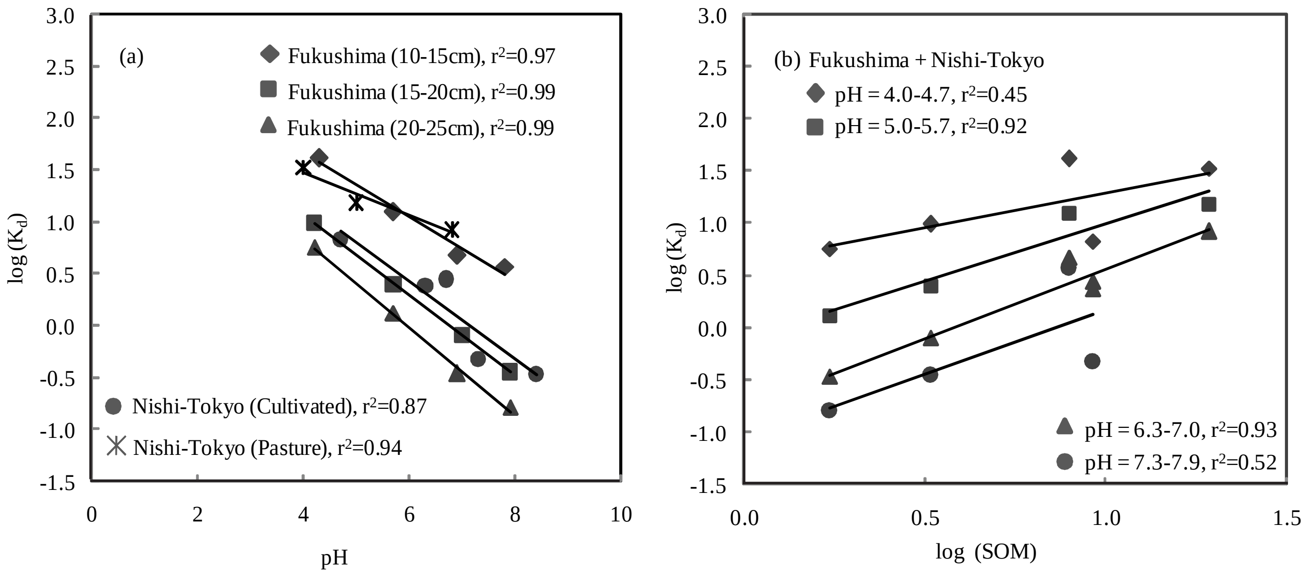


Figure 3. (a) Correlation between pH and log-transformed adsorption coefficient, log (K_d), for Japanese volcanic ash soils. (b) Correlation between log-transformed SOM, log (SOM), and log (K_d) under different pH conditions for Japanese volcanic ash soils.

Table 3. Simple correlation coefficients among log-transformed adsorption coefficient (K_d) and selected soil properties of Japanese volcanic ash soils.

	pH*	log (SOM)*	CEC†	Sand†	Silt and Clay†
log (K_d)	-0.79	0.54	0.62	-0.05	0.05
log (K_f)	-0.79	0.45	0.45	0.04	-0.04
n	-0.01	0.16	0.7	0.46	-0.46

* : obtained from all measurements

† : obtained from measurements at natural pH

almost all 2,4-D molecules should be present in the anionic form. Thus, the higher K_d values at lower pH in this study were mainly caused by the presence of pH dependent charges in volcanic ash soils (Wada and Okamura, 1980). Under lower pH conditions, typically less than the point of zero charge, positively charged active surface hydroxyls in volcanic ash soil may attract negatively charged 2,4-D molecules easily, resulting in more pronounced 2,4-D adsorption.

The log (K_d) gave a positive linear relationship with log (SOM) in each pH range [Fig. 3(b)]. Positive correlations between K_d values and SOM were also reported in previous studies for volcanic ash soils (Müller and Duwig, 2007) as well as for normal mineral soils (Nishiguchi *et al.*, 2003; Boivin *et al.*, 2005; Shareef and Shaw, 2008). The higher K_d values were observed at higher SOM, however, recent works on investigating mechanisms of 2,4-D indicated that the active surface hydroxyls, which were attached on the active metal oxides and metal SOM complexes, were the most important soil functional groups for 2,4-D adsorption onto volcanic as soil (Hiradate *et al.*, 2007).

3.2. Derivation of predicted K_d equation

Based on the results, simple correlation coefficients among adsorption coefficients [log (K_d), log (K_f), and n] and selected soil properties such as pH, log (SOM), CEC, sand content, and silt and clay content were analyzed and reported in Table 3. The log (K_d) and log (K_f) values were highly correlated with pH, log (SOM) and CEC, while the correlations of log (K_d) and log (K_f) with sand content and silt and clay content appeared to be almost zero, suggesting that the soil texture seemed to have little or no effect on 2,4-D adsorption onto volcanic ash soils as reported in the previous research on normal mineral soils (Spark and Swift, 2002).

The single and multiple regression analyses are commonly used for expressing the adsorption coefficient, K_d or log (K_d), as functions of impact parameters for adsorption studies (e.g., Hiradate and Uchida, 2004; Cea *et al.*, 2007). Based on the simple correlation analyses (see Table 3) and good linear correlations of log (K_d) with pH and log (SOM) [see Figs 3(a-b)], the dominant parameters which affect the 2,4-D adsorption can be recognized as pH, SOM, and CEC for volcanic ash soils in this study. Thus, a multiple regression analysis was carried out to derive a predictive equation for K_d as functions of the two dominant parameters, pH and SOM. The parameter, CEC, was eliminated due to the lack of measurements in the analysis. The obtained multiple regression equation can be written as:

$$\log (K_d) = 2.04 - 0.37\,\text{pH} + 0.91 \log (\text{SOM}) \quad (r^2 = 0.83) \qquad (3)$$

The absolute value of proportional constant for log (SOM) (= 0.91) was higher than that for pH (=0.37), indicating that the SOM affects the K_d value more than pH for volcanic ash soils in this study. Besides, it is noted that the multiple regression equation for the Freundlich adsorption model [Eq. (2)] was not derived due to the weak correlations of adsorption exponent, n, with soil properties (Table 3).

3.3. Tests of the predicted K_d equation against measured datasets

The predictive K_d equation [Eq. (3)] was tested against measurements both in this study and from four literatures (Bekbölet *et al.*, 1999; Nishiguchi *et al.*, 2003; Hiradate *et al.*, 2007; Müller and Duwig, 2007). Selected characteristics and measured K_d values for soils from the literatures are described in Table 4. It is noted that the original soil organic carbon contents in the literatures were converted to soil organic matter, SOM, by assuming the soil organic carbon as 58% of the SOM.

Five separate tests were done for data subsets including: (i) a total of 20 measurements for Japanese volcanic ash soils in this study, (ii) 7 measurements for volcanic ash soils from literatures (Hiradate *et al.*, 2007; Müller and Duwig, 2007),

Table 4. Selected characteristics and measured adsorption coefficients for tested soils

No	Soils	pH	SOM(%)	CEC (meq/100g)	Sand(%)	Silt and Clay(%)	Linear isotherm		Freundlich isotherm		
							K_d	r^2	K_f	n	r^2
	Volcanic ash soil (Hiradate et al., 2007)										
1	Tsukuba, Japan (Ap Horizon, Upland)	4.0	12.4	na*	19.7	80.4	26.1	0.95	35.8	0.6	0.95
2		5.0	12.4	na*	19.7	80.4	8.3	0.94	12.3	0.7	0.99
3		6.0	12.4	na*	19.7	80.4	4.1	0.94	5.9	0.8	0.99
4		7.0	12.4	na*	19.7	80.4	2.1	0.95	3.3	0.7	0.93
	Volcanic ash soils (Müller and Duwig, 2007)										
5	Mexico City, Mexico (0-14 cm, Cultivated)	6.0	7.8	35.2	na*	na*	11.3	0.98	8.8	0.9	0.99
6	Ohakune, New Zealand (0-14 cm, Cultivated)	5.0	15.5	38.2	na*	na*	10.1	0.97	6.6	0.8	0.99
7	Ohakune, New Zealand (75-85 cm, Cultivated)	6.1	5.2	23.3	na*	na*	2.2	0.97	1.9	0.9	0.99
	Turkey sandy soils (Bekbölet et al., 1999)										
8	Top soil (0-5 cm)	7.1	4.1	38.7	82.8	17.2	1.6	0.98	4.5	0.7	0.99
9	Top soil (0-5 cm)	5.6	4.6	31.3	78.4	21.6	1.6	0.98	7.4	0.6	0.99
10	Top soil (0-5 cm)	5.3	3.0	31.2	79.6	20.4	1.9	0.99	0.003	2.9	0.90
11	Subsoil (25-50 cm)	7.2	0.5	33.8	81.7	18.3	0.3	0.84	2.8	0.5	0.94
12	Subsoil (25-50 cm)	7.2	0.5	40.0	87.8	12.2	0.8	0.94	0.2	1.3	0.94
	Three surface soils (Nishiguchi et al., 2003)										
13	Brown forest Cambisol, Japan (Cultivated)	4.2	2.4	na*	52.8	47.2	2.8	0.99	4.2	0.8	0.99
14		6.1	2.4	9.5	52.8	47.2	0.4	0.98	0.9	0.8	0.99
15		6.9	2.4	na*	52.8	47.2	0.2	0.97	nd†	nd†	nd†
16		7.9	2.4	na*	52.8	47.2	0.1	0.87	0.3	0.6	0.99
17	Dystrophic Red Latosol, Brazil	3.4	0.8	na*	80.0	20.0	1.3	0.99	nd†	nd†	nd†
18		4.3	0.8	5.4	80.0	20.0	0.8	0.99	1.6	0.8	0.99
19		7.1	0.8	na*	80.0	20.0	0.1	0.99	nd†	nd†	nd†
20		7.6	0.8	na*	80.0	20.0	0.0	0.93	0.2	0.5	0.94
21	Granitic Regosol, Japan (Cultivated)	4.1	0.3	na*	71.2	28.8	0.3	0.98	0.6	0.8	0.99
22		6.3	0.3	3.4	71.2	28.8	0.0	0.82	0.2	0.6	0.99
23		7.1	0.3	na*	71.2	28.8	0.0	0.97	nd†	nd†	nd†
24		7.8	0.3	na*	71.2	28.8	0.0	0.97	0.1	0.6	0.91

* : not avaliable

† : not determined

(iii) 5 measurements for Turkey sandy soils (Bekbölet *et al.*, 1999), (iv) 12 measurements for three surface soils in Japan and Brazil (Nishiguchi *et al.*, 2003), and (v) 24 measurements for all tested soils from literatures.

Two statistical indices, RMSE and bias, were used to evaluate the performance of predictive K_d equation in Eq. (3). To evaluate the fitness of the equation against the measured data, the RMSE was used:

$$\mathrm{RMSE} = \sqrt{\frac{1}{m}\sum_{i=1}^{m} d_i^2} \qquad (4)$$

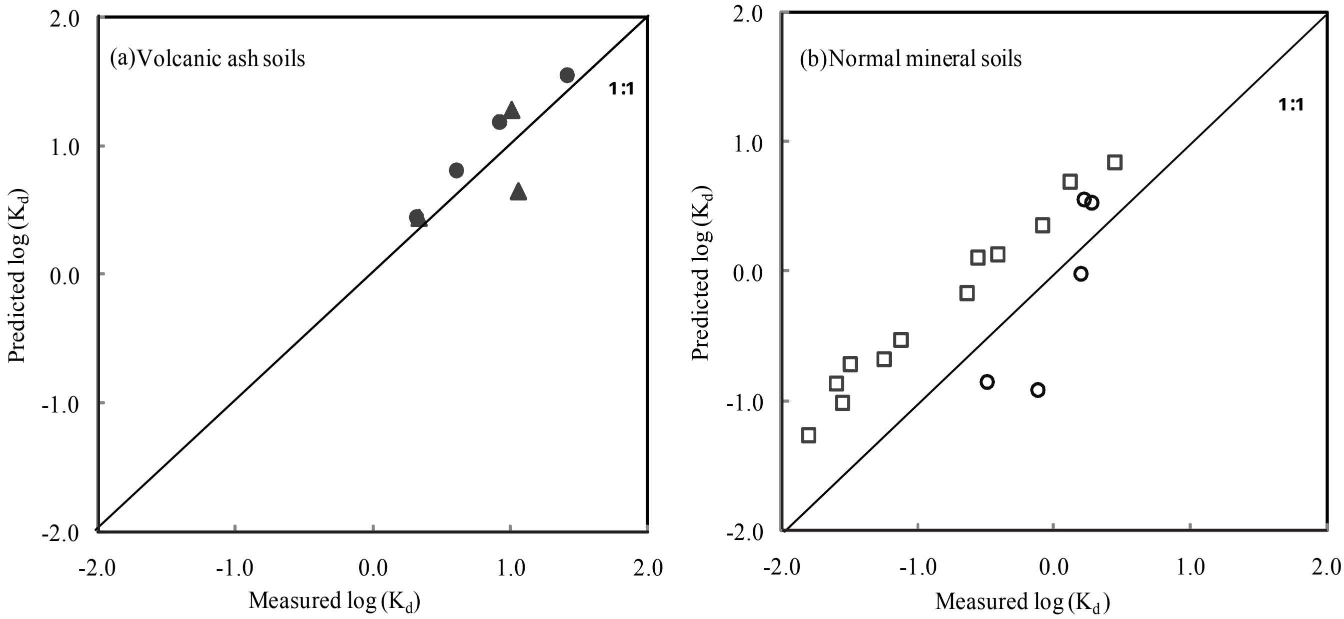
where d_i [$= \log (K_d)_{predicted} - \log (K_d)_{measured}$] is the difference between the log-transformed predicted and measured values of K_d, and m is the number of measurements. The bias was used to evaluate overestimation (positive bias) or underestimation (negative bias) of the predictive equation against measured data:

$$\mathrm{bias} = \frac{1}{m}\sum_{i=1}^{m} d_i \qquad (5)$$

The values of RMSE [Eq. (4)] and bias [Eq. (5)] were tabulated in Table 5. Scatterplot comparisons of predicted and measured log (K_d) values for volcanic ash soils from literatures and normal mineral soils (Turkey sandy soils and three surface soils) are also depicted in Figs. 4(a-b).

The predictive K_d equation [Eq. (3)] gave better predictions against measured K_d values for volcanic ash soils [Table 5 and Fig. 4(a)] and gave the best performance against volcanic ash soils from literatures among tested data subsets (RMSE = 0.239), suggesting that the proposed equation in this study is useful for predicting K_d values for 2,4-D adsorption onto volcanic ash soils. For normal mineral soils, however, the predictions gave slightly overestimation for three surface soils (bias = 0.570) and underestimation for Turkey sandy soils (bias = -0.158), indicating that the proposed K_d equation would not be applicable to predict K_d values for normal mineral soils.

The newly proposed K_d equation was simply derived by the correlation analysis of measurements in this study. It does not consider possible 2,4-D adsorption mechanisms onto volcanic ash soils and important soil components involved in 2,4-D adsorption such as solid-state organic matter, metal oxides and metal SOM complexes for developing the predictive equation (Spark and Swift, 2002; Hiradate *et al.*, 2007). Further studies are required to take adsorption mechanisms into account for the K_d prediction and to evaluate the proposed predictive K_d equation. However, the simply expressed predictive K_d equation in this study does not require detailed information on the soil texture and soil components involved in 2,4-D adsorption and seems highly useful for predicting K_d values n volcanic ash soils for practical purposes.



Volcanic ash soils (RMSE = 0.239, bias = 0.101)

● Tsukuba, Japan (Hiradate et al., 2007)

▲ Mexico & New Zealand (Műller and Duwig, 2007)

○ Turkey sandy soils (RMSE = 0.446, bias = -0.158) Turkey (Bekbölet et al., 1999)

□ Three surface soils (RMSE = 0.580, bias = 0.570) Japan & Brazil (Nishiguchi et al., 2003)

Figure 4. Scatterplot comparisons of measured and predicted log (K_d) values for (a) volcanic ash soils at different sites and countries, and for (b) normal mineral soils.

Table 5. Performance of the predictive K_d equation in Eq. (3), log (K_d) = 2.04-0.37 pH+0.91 log (SOM), against measured data in this study and measured data from literatures.

Soils	n*	RMSE	bias
Japanese volcanic ash soils (Fukushima and Nishi-Tokyo soils in this study)	20	0.270	0.010
Volcanic ash soils (Hiradate et al., 2007; Műller and Duwig, 2007)	7	0.239	0.101
Turkey sandy soils (Bekbölet et al., 1999)	5	0.446	-0.158
Three surface soils (Nishiguchi et al., 2003)	12	0.580	0.570
All tested soils (volcanic ash soils+ normal mineral soils)	24	0.475	0.281

* : number of measurements

4. Conclusions

Effects of pH and SOM on adsorption of 2,4-D onto volcanic ash soils were investigated in this study. Measured adsorption coefficients (K_d) were correlated with both pH and SOM. Based on the measured data, a predictive K_d equation for volcanic ash soils, log (K_d) = 2.04 - 0.37pH + 0.91log (SOM), was obtained by multiple regression analysis. The predictive K_d equation gave good prediction for K_d values for volcanic ash soils at different sites and countries and slightly over- or under-predicted K_d values for normal mineral soils, suggesting that the equation is promising for predictions of K_d values for volcanic ash soils.

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