広島大学大学院工学研究科研究報告，53,　1　(2004)

Bulletin of the Graduate School of Engineering, Hiroshima University. Vol. 53, No.1, 2004

Effect of Organic Carbon Content and pH on Sorption of Linuron and 2,4-D by Three Soils

Ilka NISHIGUCHI*, Per MOLDRUP**, Toshiko KOMATSU***,
Yorimitsu KODAMA* and Sotaro ITO*

The effects of organic carbon content (C_{oc}) and pH on the sorption coefficients (K_d) of linuron (non-ionic pesticide) and 2,4-D (ionic pesticide) on three surface soils have been investigated by batch equilibrium method and were found to be expressed by the equation, $\log K_d = 3.83 - 0.39\,\text{pH} + \log C_{oc}$, for 2,4-D within 24% deviation.

Key words : linuron, 2,4-D, pH, organic carbon content, sorption coefficient

1. Introduction

Understanding and predicting the degree of sorption of pesticides onto soils are one of the important fields in the environmental science and technology, since the soils play a defensive role against leakage of these pesticides into groundwater.[1,2] The degree of sorption of a pesticide on soils is usually expressed in term of sorption coefficient or distribution coefficient K_d.[3]

The effect of the soil properties such as pH, organic carbon contents (C_{oc}) and clay mineral content on the K_d values has been studied by many researchers.[4-6] It is frequently reported in the literature that organic substances in the soil effectively adsorbs non-ionized pesticides, and that when C_{oc} is relatively low, silt and clay contents have the major play in the sorption.[7,8] No correlation was found, however, between sorption coefficient of linuron and clay content of the soil in the previous study by Sánchez-Camazano et al..[9]

In spite of the extensive studies on the sorption of pesticides onto soils, a quantitative relationship between K_d and soil properties have never been reported except the correlation between K_d and C_{oc}.[2] The purposes of this study are ⅰ) to examine the effect of C_{oc} of soils as well as pH on the sorption coefficient of non-ionic (linuron, 3-(3,4-dichlorophenyl)-1-methoxy-1-methyl urea) and ionic pesticide (2,4-D, 2,4-dichlorophenoxyacetic acid), ⅱ) to formulate the observed sorption coefficient as function of C_{oc} and pH and ⅲ) to propose a method for predicting the numerical value of sorption coefficient without measurement.

2. Materials and Methods

2.1.Soils

Three surface soils were used in this experiment. 1) Granitic Regosol, truncated immature (C_{oc} = 0.0020 grams of organic carbon per gram of soil), a sandy loam soil, taken from the agricultural research field of Hiroshima University campus, 2) Brown Forest Soil (C_{oc} = 0.0141), collected at an agricultural site in the Zentsuji city, Kagawa prefecture and 3) Brazilian soil, Dystrophic Red Latosol (C_{oc} = 0.0046), an oxysol collected from Faculty of Agricultural Science, Universidade Estadual Paulista (UNESP), Botucatu city, Brazil, Soil samples were air-dried overnight, passed through a < 2.0 mm sieve and stored in sealed containers at room temperature.[9] Some physical and chemical properties of these soils are shown in Table 1.

2.2. Chemicals

Analytical grade reagents of linuron (Riedel-de Haen GmbH, Germany) and 2,4-D (Cica-reagent) were used without further purification. Stock solutions of linuron and and 2,4-D were prepared by dissolving a weighed

---

* Department of Chemistry and Chemical Engineering, Hiroshima University
** Department of Environmental Engineering, Aalborg University
*** Department of Biological and Engineering Science, Saitama University

Table 1. Selected characteristics of three soils

Properties	Dystrophic Red Latosol	Brown Forest Soil	Granitic Regosols
Textural Fractions	loamy sandy	loam	sandy loam
Clay (%)	16	12.4	9.0
Silt (%)	4	34.8	19.8
Sand (%)	80	52.8	71.2
Organic carbon content (g-carbon.g-soil^{-1})	0.046	0.0141	0.0020
CEC (meq.100 g^{-1})	5.4	9.50	3.40
Bulk density (g.cm^{-3})	1.5	1.43	1.68
Water content (cm^3.cm^{-3})	0.28	0.37	0.21
pH (1:2.5 H_2O)	4.6	6.0	6.5
pH (1:2.5 KCl 1 M)	4.1	4.7	4.5
pH (1:2.5 $CaCl_2$ 0.01 M)	4.3	5.3	5.1

amount of these pesticides in 100 mL of 0.005 M $CaSO_4$ to yield a final concentration of 50 mg.L^{-1}. The solutions were kept in the laboratory bottle with screw-cap and stored at 5°C. The physical and chemical properties of the pesticides are summarized in Table2. The toxicity class according to EPA are III for linuron and II for 2,4-D.[10)]

2.3. Batch sorption measurement

All measurements of sorption were made in duplicate. A standard procedure for batch sorption experiments is as follows. For the kinetic experiments, 10 g of soils (Brown Forest Soil and Granitic Regosol) was weighed into conical flask of 100 mL, and 10 mL of linuron solution of 50 mg.L^{-1} was added. The flasks were shaken for 0.5-96 h at 25±1°C on a rotary shaker at 50-60 rpm. At termination, the soil-water suspension was allowed to settle for 10 to 15 min. Subsequently, the suspensions were centrifuged at 12,000 rpm for 10 min and an aliquot of the supernatant was then filtered through a 0.2 µm cellulose acetate membrane filter (ADVANTEC). The filtrate was directly injected into a highperformance liquid chromatography (HPLC) for the determination of the concentration (C_w) of linuron in the solution.

Experiments for sorption isotherm were conducted with the same procedure as described above with a shaking period of 24 h. The isotherms for linuron were constructed at six initial concentrations ranging from 0.25 to 50 mg.L^{-1} for sorption at native soil pH, and at four initial concentrations ranging from 5.0 to 40 mg.L^{-1} for sorption at pH 4.0 – 7.9 adjusted with diluted HCl or NH_4OH. The sorbed concentration (C_s) of the pesticide was calculated by the following equation for each sample and reported as time-function :

$$C_s = V\,(C_i - C_e)/\,M$$

where C_s (mg.kg^{-1}) is the adsorbed fraction of pesticide in soil, C_i (mg.L^{-1}) is the initial concentration of pesticide in the liquid phase, C_e (mg.L^{-1}) is the pesticide concentration in the liquid phase after equilibrium, V (L) is the total volume of solution added to the conical flask and M (kg) is the weight of the soil used.

The sorption experiments for 2,4-D were done likewise with the procedure described above.[9)]

2.4. Analytical procedure

HPLC analysis was done with Shimadzu LC-10A on Mightysil RP-18 GP 5 µm 150 x 4.6 column at detection wavelength of 244 nm. The injected volume was 20 µL and the flow rate was set at 1.0 mL.min^{-1} with eluent of 60:40 v/v acetonitrile/ milli-Q water. The retention time for linuron under these conditions was approximately 6.7±0.098 min and the detection limit was 0.25 mg.L^{-1}. The analytical precision was ±0.67% based on standard samples.

The organic carbon content (C_{oc}, in grams of organic carbon per gram of soil) of the soils was determined using a CN analyzer (MT-700, Yanako CN Corder,

Table 2. Physical and chemical properties of linuron and 2,4-D

Compound	Solubility in water at pH 7 (mg.L^{-1})	log K_{ow}	pKa	Mol. weight	Half life time in soil (days)	Vapor pressure (mPa)
Linuron	63.8 (20°C)	3.0	---	249.1	38 - 67	0.051(20°C)
2,4-D	23,180 (25°C)	2.7(pH 1)	2.73	221.0	< 7	0.019 (25°C)

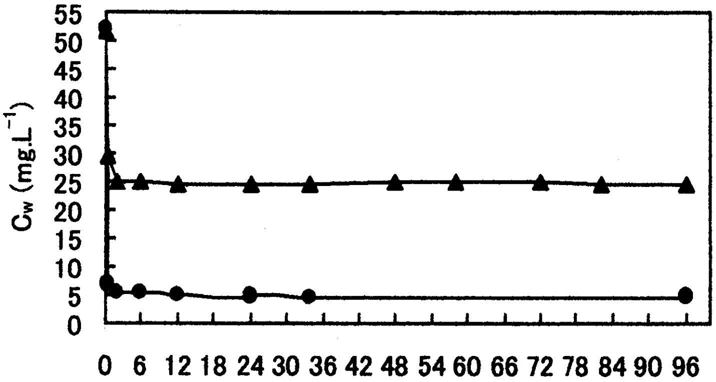

Figure 1. Kinetics of linuron adsorption measured in Brown Forest Soil (●) and in Granitic Regosol (▲)

Kyoto, Japan), assuming that the observed carbon content reflects organic carbon content.[11)]

3. Results and Discussion

3.1. Sorption kinetics and isotherms

The kinetic data for Brown Forest Soil and Granitic Regosol, characterized by declining liquid phase concentration (C_w) as a function of time over a 4-day period are presented in Figure 1. The sorption equilibrium of linuron was achieved within 6 h, as shown in Figure 1, while 24 h were necessary to reach a sorption equilibrium for 2,4-D.[9)] Based on the sorption kinetics for Brown Forest Soil and Granitic Regosol, the sorption kinetic for Red Latosol was estimated to be very similar. The kinetics experiment revealed that the contact for 24 h is enough to reach the for equilibrium.

All sorption isotherms were adequately described by Freundlich equation (1) with correlation coefficient (R^2) values greater than 0.99 (Table 3).

$$C_s = K_f C_e^n \qquad (1)$$

where C_s is the sorbed concentration (mg.Kg^{-1}), C_e is the equilibrium concentration in the solution (mg.L^{-1}), K_f is Freundlich sorption oefficient and n is a power function related to the sorption mechanism or intensity. When n = 1, equation (1) becomes linear equation (2),

$$C_s = K_d C_e \qquad (2)$$

in which K_d is the sorption coefficient (L.kg^{-1}). Compilations of sorption data for many organic compounds[12)] indicated that the n values for pesticide sorption generally range between 0.75 and 0.95. Though the Freundlich equation can well describe the relation between C_s and C_e, it is difficult to compare the relative values of K_f which have different n values in equation (1), since the K_f with different n values has different units to each other. Accordingly, the linear sorption coefficient K_d was used throughout this study.

3.2. Sorption coefficient (K_d) of linuron at various pH

The K_d values of linuron sorption obtained for three soils at different pH are summarized in Table 4. In general, the K_d of linuron scarcely depends on pH of the

Table 3 Freundlich sorption coefficients (K_f), n and R^2 of linuron and 2,4-D at various pH for three soils.

soil	Linuron				2,4-D			
	K_f (L.kg^{-1})	n	R^2	pH	K_f (L.kg^{-1})	n	R^2	pH
Brown Forest Soil	13.96	0.77	0.999	4.1	4.21	0.83	0.999	4.2
	11.16	0.82	0.999	6.0*	0.94	0.75	1	6.1*
	9.37	0.87	0.997	7.8	0.33	0.59	0.999	7.9
Dystrophic Red Latosol	4.02	0.84	0.997	4.0*	1.61	0.80	1	4.3*
	4.41	0.80	0.991	7.8	0.15	0.48	0.944	7.6
Granitic Regosol	1.71	0.80	0.999	4.0	0.61	0.79	0.999	4.1
	1.39	0.84	0.999	6.0*	0.16	0.57	0.987	6.3*
	1.36	0.81	0.996	7.9	0.06	0.58	0.91	7.8

*native soil pH at equilibrium sorption

Table 4. Sorption coefficient of linuron on three soils at different pH conditions

Soil	K_d (L.kg^{-1})	R^2	K_{oc} (L.kg^{-1})	pH
Brown Forest Soil	10.62	0.968	753	4.1
(C_{oc} = 0.0141)	8.38	0.981	594	6.0*
	7.79	0.987	552	7.8
Dystrophic Red Latosol	2.65	0.986	576	4.0*
(C_{oc} = 0.0046)	2.79	0.925	606	7.8
Granitic Regosol	0.95	0.975	473	4.0
(C_{oc} = 0.0020)	0.83	0.986	414	6.0*
	0.78	0.973	389	7.9

* native soil pH at sorption equilibrium

solution. The effect of soils on K_d for linuron was, on the contrary, significant and the K_d values increased with increasing C_{oc}. The order of the magnitude of K_d is,

K_d (Brown Forest Soil) > K_d (Dystrophic Red Latosol) > K_d (Granitic Regosol)

3.3. Sorption coefficient (K_d) of 2,4-D at various pH

The effect of pH on sorption was more pronounced for 2,4-D than for linuron on three soils, as shown in Table 5. This is in accordance with the results of Baskaran et al.[6] for non-ionic and ionic herbicides on allophanic and non-allophanic soils.

Figure 2 shows the plots of log K_d against pH for 2,4-D and linuron on Brown Forest Soil (A) and Granitic Regosol (B). The linear correlation between log K_d and pH for both linuron and 2,4-D is evident in these figures, indicating that the equation (3) holds between K_d and the concentration of H^+ ions,

$$K_d = k[H^+]^m \qquad (3)$$

where k is a constant for given pesticide and soil. The logarithmic form of equation (3) gives equation (4),

$$\begin{aligned} \log(K_d) &= \log k + m \log[H^+] \\ &= \log k - m\,\mathrm{pH} \qquad (4) \end{aligned}$$

The values of m in equations (4) can be determined from the slopes in Figure 2 and are equal to – (0.39±0.04) for 2,4-D and – (0.018±0.020) for linuron.

3.4 Effect of C_{oc} on K_d of linuron and 2,4-D

The effect of exogenous carbon sources on K_d values for sorption and movement of ionic pesticide (2,4-D and atrazine) has been demonstrated by Baskaran (1996) , where the addition of organic waste materials increased the K_d of 2,4-D and atrazine.

Since C_{oc} of the soil is correlated well with pesticide sorption in most studies, the use of the organic carbon sorption coefficient (K_{oc}) was proposed by Hamaker and Thompson.[11] The organic carbon sorption coefficient K_{oc} is obtained by dividing the K_d values of soils by C_{oc},

Table 5. Sorption coefficient of 2,4-D on three soils at different pH conditions

Soil	K_d (L.kg^{-1})	R^2	K_{oc} (L.kg^{-1})	pH
Brown Forest Soil	2.76	0.993	196	4.2
(C_{oc} = 0.0141)	0.386	0.976	27.4	6.1
	0.232.	0.965	16.5	6.9
	0.075	0.872	5.3	7.9
Dystrophic Red Latosol	1.32	0.991	287	3.4*
(C_{oc} = 0.0046)	0.828	0.988	180	4.3
	0.057	0.996	12	7.1
	0.025	0.925	5.4	7.6
Granitic Regosol	0.278	0.979	139	4.1
(C_{oc} = 0.0020)	0.032	0.823	16	6.3
	0.028	0.970	14	7.1
	0.016	0.970	8.0	7.8

* native soil pH at sorption equilibrium

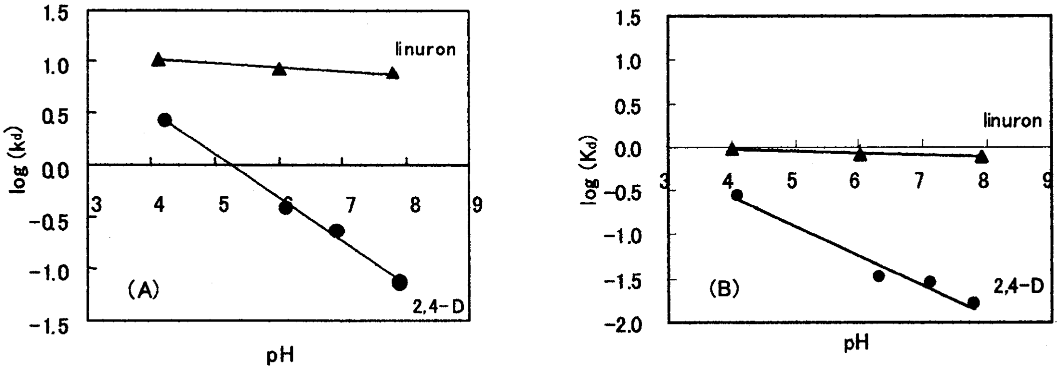

Figure 2 Logarithmic plots of K_d against pH on Brown Forest Soil (A) and Granitic Regosol (B).

$$K_{oc} = K_d / C_{oc} \qquad (5)$$

In the present study, the observed K_d values were, in accordance with equation (5), proprtional to the C_{oc} of the soils for linuron and 2,4-D at a constant pH. The values calculated from equation (5) for each soil are summarized in Tables 4 and 5.

Inspection of the data listed in Table 4 for linuron indicates that the variation in K_{oc} was very small in comparison with one found in original K_d values. The variation found in K_{oc} of 2,4-D was significant, indicating that the effect of pH on K_d overcomes the one of C_{oc} on K_d. This trend agrees with the results of Barriuso et al.$^{5)}$, which showed the non-ionic pesticide (atrazine) gave the essentially constant K_{oc} values (56±16 $L.kg^{-1}$), while the K_{oc} values of terbutryn (weakly basic pesticide) and 2,4-D (acidic pesticide) ranged from 179 to 468 $L.kg^{-1}$ and from 24 to 685 $L.kg^{-1}$, respectively.

Taking account of the facts that the K_{oc} values of linuron are essentially constant for three soils (Table 4), plots of $\log(K_{oc})$ against pH are tentatively done and shown in Figure 3, which demonstrate approximately linear relationship between $\log(K_{oc})$ and pH for 2,4-D as well as for linuron. The linearity observed in Figure 3(B) for 2,4-D is quite attractive, since K_{oc} has been believed not to be constant in the sorption of ionic pesticides for a long time. The least square method gives the equation (6) and (7) from the plots in Figure 3 for linuron and 2,4-D, respectively.

$$\log(K_{oc}) = 2.83 - 0.018\text{pH} \qquad (6)$$

$$\log(K_{oc}) = 3.83 - 0.39\text{pH} \qquad (7)$$

Using the logarithmic form of equation (3), $\log(K_{oc}) = \log(K_d) - \log C_{oc}$ linuron and 2,4-D, one can obtain equations (8) and (9) for linuron and 2,4-D, respectively.

$$\log(K_d) = 2.83 - 0.018\text{pH} + \log C_{oc} \qquad (8)$$

$$\log(K_d) = 3.83 - 0.39\text{pH} + \log C_{oc} \qquad (9)$$

From the equations (8) and (9), one can calculate the

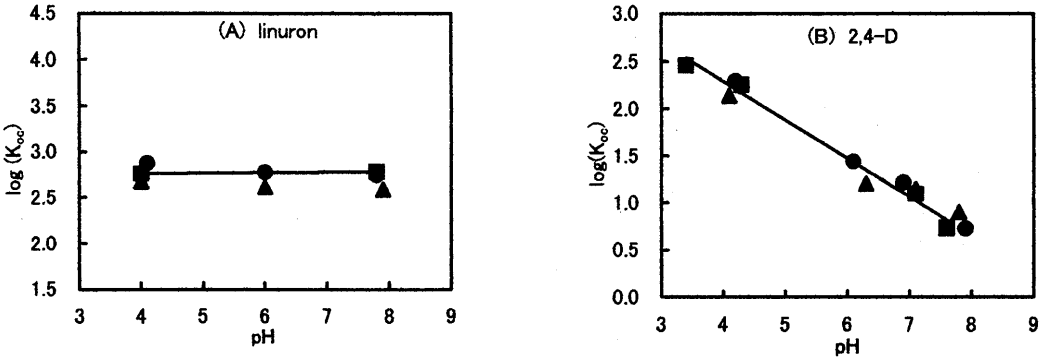

Figure 5 Logarithmic plot of sorption coefficient () against pH for (A) linuron and (B) 2,4-D.
●: Brown Forest Soil, ■: Dystrophic Red Latosol, ▲: Granitic Regosol

Table 6 Comparison of the Value of Observed Sorption Coefficient $(K_d)_{obs}$ with $(K_d)_{calc}$ Calculated from Equations (8) and (9) for Sorption of Linuron and 2,4-D at Various pH

Pesticide	Soil	pH	$(K_d)_{obs}$	$(K_d)_{calc}$ [a)]	$(K_d)_{calc}/(K_d)_{obs}$
Linuron	Brown Forest Soil	4.1	10.62	8.06	0.76
		6.0	8.38	7.45	0.89
		7.8	7.79	6.91	0.89
	Dystrophic Red	4.0	2.65	2.62	0.99
		7.8	2.79	2.24	0.80
	Granitic Regosol	4.0	0.95	1.14	1.20
		6.0	0.83	1.05	1.27
		7.9	0.78	0.97	1.24
	Average ± Standard	Deviation			1.01 ± 0.20
Pesticide	Soil	pH	$(K_d)_{obs}$	$(K_d)_{calc}$ [b)]	$(K_d)_{calc}/(K_d)_{obs}$
2,4-D	Brown Forest Soil	4.2	2.76	2.20	0.80
		6.1	0.386	0.40	1.04
		6.9	0.232	0.19	0.82
		7.9	0.075	0.079	1.05
	Dystrophic Red Latosol	3.4	1.32	1.46	1.11
		4.3	0.828	0.65	0.79
		7.1	0.057	0.053	0.93
		7.6	0.025	0.034	1.36
	Granitic Regosol	4.1	0.278	0.34	1.22
		6.3	0.032	0.047	1.47
		7.1	0.028	0.023	0.82
		7.8	0.016	0.012	0.75
	Average ± Standard	Deviation			1.01 ± 0.24

a) Calculated from Equation (8).
b) Calculated from Equation (9).

values of sorption coefficient $(K_d)_{calc}$ using the numerical values of pH and C_{oc} given in Tables 4 and 5. The $(K_d)_{calc}$ values obtained from the equations (8) and (9) are summarized in Tables 6. The relative ratios of $(K_d)_{calc}$ to the observed values of sorption coefficient $(K_d)_{obs}$ are approximately unity with the standard deviations within 24%.

The agreement of $(K_d)_{calc}$ with $(K_d)_{obs}$ demonstrated in Table 6 for 2,4-D indicates that the concept of K_{oc} is useful for the sorption of ionic pesticides as well as non-ionic ones.

4. Conclusions

The examination of the effect of the organic carbon content (C_{oc}) on the sorption coefficient (K_d) of linuron and 2,4-D onto three soils at different pH revealed that the sorption of linuron on these soils is directly related to C_{oc}. For the sorption of 2,4-D (anionic pesticide), the K_d value can be expressed as a function of pH and C_{oc},, i.e., $\log (K_d) = 3.83 - 0.39\text{pH} + \log C_{oc}$, indicating that the concept of the organic carbon sorption ($K_{oc}=K_d/C_{oc}$) is useful for the sorption of ionic pesticides as well as non-ionic ones.

Acknowledgements

We are grateful to Dr. Kenji Kouno, from Dept. of Soil Science and Plant Nutrition, Faculty of Applied Biological Science, Hiroshima University, for having kindly provided the measurement of organic carbon content.

References

1) Sparks, Donald L., Sorption Phenomena on Soils in "Environmental Soil Chemistry", Academic Press, pp99-139 (1995).
2) Watson, Jack E., Pesticides as a Source of Pollution in "Pollution Science", Academic Press, pp253-266 (1996).
3) Matthess, G., Fate of Pesticides in Aquatic Environments in "Pesticides in Ground and Surface Water" (Vol. 9) , Borner, H. (Volume Editor), Springer-Verlag, pp191-246 (1994).
4) Reddy, K. S., Gambrell, R. P., Agric. Ecosys.

Environ., 18, 231-21 (1987).
5) Barriuso, E., Feller, Ch., Calver, R., Cerri, C., Sorption of atrazine, terbutryn and 2,4-D herbiides in two Brazilian Oxisols, Geoderma, 53, 155-167 (1992).
6) Bakaran, S., Bolan, N. S., Rahman, A., and Tillman, R. W., Aust. J. Soil Res., 34, 609-622 (1996).
7) Worral, F., Parker, A., Rae, J.E. Johnson, A.C., Equilibrium adsorption of isoproturon on soil and pure clays, Europ.J. Soil Sci., 47, 265-272 (1996).
8) Sánchez-Martín, M.J., Rodríguez-Cruz, M.S., Sánchez-Camazano, M., Study of the desorption of linuron from soils to water enhanced by the addition of an anionic surfactant to soil-water system, Water Res., 37, 3110-3117 (2003).
9) Nishiguchi, I., Kodama, Y., Komatsu, T., Ito, S., The Effect of pH on Sorption of 2,4-D on Three soils, Environ. Eng. Res., vol. 40, 697-703 (2003).
10) Tomlin CDS (Ed), “The Pesticide Manual”, Twelfth edition, Surrey, UK : British Crop Protection Council (2000).
11) Regitane, J. B., Alleoni, L. R. F., Vida-Torrado, p., Casagrande, J. C., and Tornisielo, Imazaquin Sorption in Highly Weathered Tropical Soils, J. Environ. Qual., 29, 894-900 (2000).
12) Hamaker, J. W. and Thompson, J.M., Adsorption, in “Organic Chemicalsin the Soil Environment”, C.A.I. Goring and J. W. Hamaker (Editors), Marcel Dekker, New York, pp51-14 3(1972).

(Received September 30, 2004)