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Original Article

Adsorption Rate Equation of Herbicides in Paddy Soils

Kaori KIBE,* Makoto TAKAHASHI, Takashi KAMEYA and Kohei URANO

Faculty of Engineering, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

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It is vital not to under evaluate the adsorption rates of paddy herbicides, which influence their movement in the soil and water for environmental safety and agricultural practice. The adsorption rates of four herbicides, esprocarb, thiobencarb, pretilachlor and simetryn, in three kinds of paddy soil whose properties varied widely were investigated. It was found that the herbicides were absorbed in the soils in two steps characterized by fast and slow phases. The ratios of the fast adsorption α were independent of the initial concentration for each tested system of herbicide and soil. Then an adsorption rate equation was introduced from α and the approximated Boyd equation and its applicability was confirmed. The rate parameters of the slow adsorption D_i'/r^2 were obtained in the range of 3.4×10^{-7} to 7.3×10^{-7}/s by the proposed equation. The differences among the herbicides and the soils were small.

Key words: paddy herbicides, paddy soils, adsorption, rate equation.

INTRODUCTION

Rice cultivation in paddy fields is very common in South East Asia including Japan, but it is feared that paddy herbicides cause environmental pollution because they are used in large quantities under flooded conditions.[1-4] So, predicting the fate of herbicides in paddy soil, water is necessary for environmental safety and agricultural practice, and it is important to know the adsorption characteristics of herbicides in the soil where they remain for a long time. For example, the leaching and runoff characteristics of herbicides are highly expected to be changed with the adsorption rates.[5]

In many conventional fate models for pesticides registration,[6-9] however, the pesticide concentrations have been calculated with the assumption that their adsorption rates are very fast and pesticides immediately adsorb into the soil to the equilibrium.

In this research, the adsorption rates of four paddy herbicides in three kinds of soil found in Japan were investigated and an adsorption rate equation, based on the two step adsorption of a fast phase and a slow phase was derived. Further, the ratios of the fast phase and the rate parameters of the slow phase were obtained and discussed in relation to their correlation to the properties of soil and herbicides.

MATERIALS AND METHODS

1. *Paddy Herbicides*

Esprocarb, pretilachlor, simetryn and thiobencarb which are used in large amounts in the paddy fields of Japan[1-4] were examined in this study. The standard reagents of pretilachlor by Kanto Chemicals Ltd., and esprocarb, simetryn and thiobencarb by Wako Chemicals Ltd. were used as solutions in acetone. The chemical and physical properties of the four herbicides are shown in Table 1.[2-4] The values of Pow and the solubilities in water differ about 100 times, and the literature data of Koc also differ about 2 times among the tested four paddy herbicides.

2. *Soil Samples*

Three kinds of soil from the test paddy fields of the agricultural experiment stations in Niigata, Hyogo and Kumamoto Prefectures were used in this study. They are ones of the popular areas for producing rice and together they represent different agricultural conditions. They were collected from five or more places in the cultivated layer of the paddy fields before flooding conditions. They were mixed sufficiently and passed through a 2 mm sieve before use. Their water contents were in the range of 30% to 42%. The characteristics of these soil samples are shown in Table 2. Their organic carbon contents, surface areas and cation exchange capacities (CEC) differ about 3 times, 5 times, and 4 times from

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* To whom correspondence should be addressed.

each other, respectively.

3. *Adsorption Procedure*

Undried soil samples of 2 g or 5 g, as dry weight soil bases, were put into 300 ml Erlenmeyer flasks, and pure water which had been prepared by desalination with ion-exchange resins and purification adsorption with an activated carbon, was added to each flask until the sum of the water in the undried soil and the added water became 100 ml. This amounts of soil and water were determined to obtain their sufficient mixing conditions and proper concentration change with the adsorption. The soil samples were mixed well with a glass rod and shaken for about 1 hr to homogeneity. Then, the acetone solutions of the four herbicides were added, with a microsyringe, to the concentrations of 0.1 mg/l and 2 mg/l, and the flasks were sealed with caps. The initial concentration, 2 mg/l, corresponds to the applied amount of 100 g ai/10 a in paddy water which is 5 cm deep, and another initial concentration, 0.1 mg/l, corresponds to its one twentieth. The flasks were shaken sufficiently for 0.5, 2, 8, 24, 48, and 72 hr by a shaker machine with 85 shakes per a minute (spm) under a dark condition at 25±1°C. pH values of the suspension of soil under the test conditions were 5.7 for Niigata, 5.8 for Hyogo and 6.7 for Kumamoto, in which simetryn with p*K*a 4.0 was little ionized. The electric conductivities of the suspension of soil under the test conditions were in the range of 0.024 dS/m to 0.056 dS/m which are average values.

After shaking, the suspension was centrifuged for 15 min with 5000 rpm (4500 G), and 20 ml of the supernatant was taken and filtered by a glass fiber filter whose particle capture was 0.4 mm.

Table 1 Properties of paddy herbicides tested.[2-4]

Herbicides	Molecular weight	Solubility in water* [mg/l]	$\log P_{ow}$**	K_{oc} [ml/g]
esprocarb	265.4	4.9	4.60	580
thiobencarb	257.8	30	3.42	676
pretilachlor	311.9	50	4.08	628
simetryn	213.2	450	2.60	333

* 20°C around neutrality, ** Octanol-water partition coefficient.

4. *Analytical Method*

A 5 ml of *n*-hexane was added into the filtrate in a 50 ml centrifuge tube, and the herbicide were extracted from the filtrate by hand shaking for 30 sec. Due to a little low extraction efficiency of *n*-hexane for simetryn whose solubility in water is high, 7 g of NaCl was added before the extraction to obtain the salting-out effect. In cases where an emulsion was formed after the hand shaking, the shaken samples were centrifuged for 15 min to generate the *n*-hexane phase from the water phase. The *n*-hexane phase was collected with a pipette to a 10 ml centrifuge tube. Then, another 5 ml of *n*-hexane was added to the remaining water phase, and extracted once again by shaking in the same manner as described above. The combined *n*-hexane extract was concentrated to 0.20–2.0 ml gently by N_2 gas purging. The concentrated extract was analyzed by a FTD-GC (Shimadzu GC-17A) with a column of DB-1(0.53 mmϕ ×30 m) under the following conditions: the column temperature was programmed to be from 200°C to 250°C for 2.5 min at 20°C/min after keeping for 4 min at 200°C, the injection temperature and the detector temperature were 290°C, and the injection volume was 2 μl.

The recoveries in the extraction of each herbicide from water by the above method were examined twice and obtained as 100% for esprocarb, 91% for pretilachlor, 96% for simetryn and 90% for thiobencarb, respectively.

5. *Calculation of Adsorbed Amount*

The adsorbed amount on soil Q (mg/kg-dry) was calculated by the following equation (1) from the concentration in water C (mg/l).

$$Q=(M-CV)/W \qquad (1)$$

Where M (mg) is the amount of herbicide added, V (l) is the volume of water: 0.100, W (kg-dry) is the weight of soil: 2×10^{-3} or 5×10^{-3}.

The adsorption equilibrium had been obtained in a previous report,[10] and they were expressed by the Freundlich type equation $Q_e=kC^{1/n}$. It had been confirmed by other experiments that degradation of the tested herbicides could be neglected for 72 hr within the testing period.

Table 2 Characteristics of paddy soils used.

Location	Classification	Main clay mineral*	Particle size distribution (%) Sand	Silt	Clay	Organic carbon (%)	Supecific surface area (m^2/g)	pH in H_2O	CEC (meq/100 g)
Niigata	Gley soil	M	69	17	14	2.1	17	5.3	29.0
Hyogo	Gray Lowland soil	K	46	29	25	1.2	6.2	5.3	12.0
Kumamoto	Andosol	A	27	46	27	6.8	34	6.3	45.2

* A: allophane, K: kaolinite, M: montmorillonite.

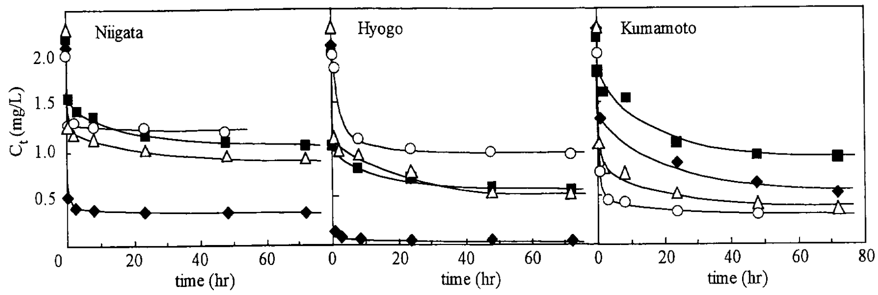

Fig. 1 Changes of herbicide concentrations in water by using Niigata, Hyogo and Kumamoto soils at initial concentration of 2 mg/l.
○: esprocarb, △: thiobencarb, ■: pretilachlor, ◆: simetryn.

RESULTS AND DISCUSSION

1. Two Step Adsorption of Herbicides

The changes of concentrations of esprocarb, pretilachlor, simetryn and thiobencarb in water with adsorption by Niigata, Hyogo and Kumamoto soils are shown in Fig. 1. It was confirmed that the tested four herbicides reached their adsorption equilibriums within 72 hr, because no decreases in herbicide concentrations were observed after that. The period it took to reach each equilibrium was almost the same as the previous studies.[10–12] Furthermore, it was found that for every tested system, a part of the adsorption occurred quickly, within about 30 min of the beginning (fast phase), then reached slowly to the equilibrium (slow phase). This phenomenon was first reported by Huang and Liao in 1970[13] and recently reported for adsorption of isoproturon[14] and atrazine.[14,15] But there is no studies on the effect of the initial concentrations for various systems of herbicide and soil and on the rate equation of the two step adsorption.

Then increases in adsorbed amounts at different initial concentrations of 0.1 mg/l and 2 mg/l were examined for the systems of the same herbicide and the same soil. The results for the system of the Niigata paddy soil and pretilachlor is shown in Fig. 2, as an example. The adsorption by two steps of the fast phase within 30 min and the slow phase for a longer time afterward were recognized at each concentration. The increases of the overall adsorption ratio F, which is defined as a ratio of the adsorbed amount at each time Q_t to the equilibrium adsorbed amount Q_e, are also shown in Fig. 2 for the same system. Though the initial concentrations differ by 20 times, the values of F were almost the same. This fact was confirmed for every tested system of herbicide and soil.

Consequently, the assumption used in many conventional fate models that all the pesticides quickly adsorb into the soil to the equilibrium is not correct, and the slow adsorption rate should be considered when the value of F becomes larger than the fast adsorption ratio α, which is obtained as the ratio of the quickly adsorbed amount to the equilibrium adsorbed amount Q_e.

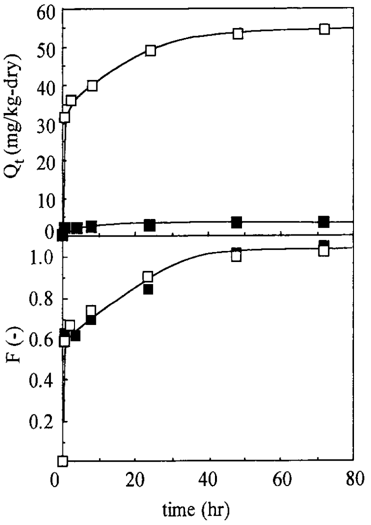

Fig. 2 Adsorption rates of pretilachlor on Niigata soil at different initial concentrations of 0.1 mg/l and 2 mg/l.
closed black plot: 0.1 mg/l, open plot: 2 mg/l.

2. Adsorption Rate Equation

Since the adsorbed amount of the fast phase is αQ_e, the adsorbed amount with the slow phase at time t is expressed as $Q_t-\alpha Q_e$, and it reaches the equilibrium value of $(1-\alpha)Q_e$ slowly. On considering the slow phase of adsorption, the adsorption ratio $F_{\rm II}(-)$ at time t is expressed as equation (2).

$$F_{\rm II}=(Q_t-\alpha Q_e)/(1-\alpha)Q_e \tag{2}$$

Then this is further transformed to equation (3) for the overall adsorption ratio F $(-)$.

$$F=Q_t/Q_e=(1-\alpha)F_{\rm II}+\alpha \tag{3}$$

Because terms longer than 24 hr were needed to reach the equilibrium with sufficient mixing at many tested systems, slow adsorption is thought to be controlled by the intraparticle diffusion rate in the soil. The adsorption rate in a complete mixing vessel under the conditions of intraparticle diffusion control can be expressed by the following equation (4) at a constant temperature.[16]

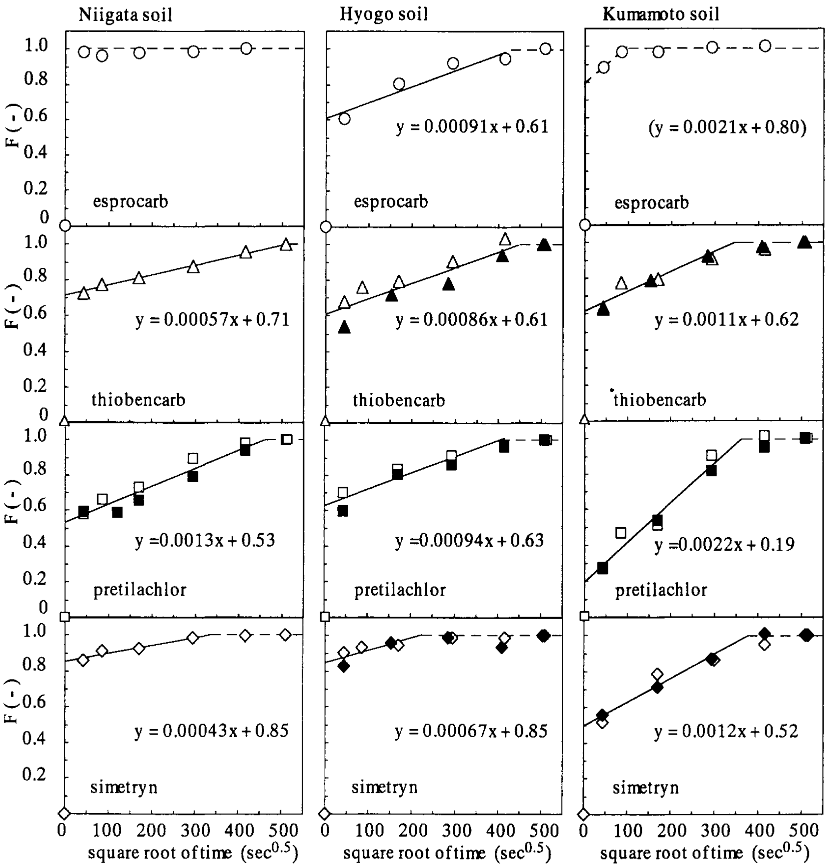

Fig. 3 Relationship between $t^{0.5}$ and overall adsorption ratio F of four herbicides in three paddy soils. Initial concentration; closed black plot: 0.1 mg/l, open plot: 2 mg/l.
○: esprocarb, △: thiobencarb, □: pretilachlor, ◇: simetryn.

$$F_{II}=1-\frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-\frac{\pi^2 D_i' n^2 t}{r^2}\right) \qquad (4)$$

Where, D_i'(cm^2/sec) is a intraparticle diffusion coefficient based on the solid concentration, t (sec) is time, and r (cm) is an effective radius of soil particles which is approximated as uniform globular particles. The equation (4) could be approximated with equation (5).[16)]

$$F_{II}=\frac{6}{r}\sqrt{\frac{D_i' t}{\pi}} \qquad (5)$$

When this is substituted for equation (3), the adsorption rate is shown as equation (6) for F.

$$F=\frac{6(1-\alpha)}{r}\sqrt{\frac{D_i' t}{\pi}}=\alpha\left\{3.39(1-\alpha)\sqrt{\frac{D_i'}{r^2}}\right\}\sqrt{t}+\alpha \qquad (6)$$

Namely, the overall adsorption ratio F should increase lineally with the square root of time t. The values of α may be obtained from the intercept of the figures of $t^{0.5}$ vs. F, and the adsorption rate parameter D_i'/r^2 may be obtained from the inclination of the figures and the value of α.

The relationships of $t^{0.5}$ to F of the four herbicides in the three soils are shown in Fig. 3. Since linear relationships were obtained, it was proved that equation (6) could be applied to the adsorption of herbicides into the paddy soil in a mixing vessel.

3. *Parameters of Rate Equation*

Because the same relationships were observed in Fig. 3 for the different concentrations of 0.1 and 2 mg/l, the values of α and D_i'/r^2 were obtained for each system of soil and herbicide. They are summarized in Table 3.

The values of α were in a wide range of 0.19 to 1.0. The systems of esprocarb and Niigata and Kumamoto soils, and the systems of simetryn and Niigata and Hyogo soils had large values of α from 0.80 to 1.0. In these systems, almost all the herbicides were adsorbed within a short time. Thiobencarb had α of 0.66 ± 0.05 in the tested soils and pretilachlor had various α in the soils.

Since it had been expected that fast adsorption may occur on the outer sites of the soil[13)] or organic substances in the soil, and that slow adsorption may occur in the micro-pores of the soil, the relationships between the values of α and the clay contents or the organic carbon contents of the soil were examined. However, no general tendency was recognized though the clay contents differed by about 2 times, and the organic carbon contents varied by 6 times in the range of 1.2 to 6.8%. This result confirmed that there was no relationship between

Table 3 Values of α and D_i'/r^2 for each system of herbicide and soil.

Soils	Herbicides	$\alpha(-)$	D_i'/r^2(1/sec)
Niigata	esprocarb	1.0	—
	thiobencarb	0.71	3.4×10^{-7}
	pretilachlor	0.53	6.7×10^{-7}
	simetryn	0.85	—
Hyogo	esprocarb	0.61	4.8×10^{-7}
	thiobencarb	0.61	4.2×10^{-7}
	pretilachlor	0.63	5.6×10^{-7}
	simetryn	0.85	—
Kumamoto	esprocarb	0.80	—
	thiobencarb	0.62	7.3×10^{-7}
	pretilachlor	0.19	6.4×10^{-7}
	simetryn	0.52	4.6×10^{-7}

—: not calculated when α is larger than 0.80.

the parameter k of the equilibrium equation and the organic carbon content.[10] Therefore, fast adsorption of herbicides does not always occur on the outer sites or on organic substances in the soils. The correlations of α with the surface area, the CEC, pH under the tested conditions and the main clay minerals of the soils were also examined. Kumamoto soil with higher pH had smaller α than the other soils, but it was considered that this difference was not caused by the difference of pH, because simetryn is little ionized under all the tested pH from 5.8 to 6.7. Any general correlation with the other properties of the different soils was not found. Furthermore, any general correlation with the values of P_{ow} and solubilities in water of the herbicides was not recognized.

On the other hand, the values of D_i'/r^2 for the slow adsorption were found to be in the range of 3.4×10^{-7}/sec to 7.3×10^{-7}/sec as shown in Table 3. The correlation of the values of D_i'/r^2 with the physical and chemical properties of the soil samples such as organic carbon contents, surface areas, CEC, pH, and clay mineral components were examined, but any general correlation was not found.

Besides, the values of D_i'/r^2 of the four herbicides varied very little from each other, and any correlations with the properties of herbicides was not recognized, though their P_{ow} values and solubilities in water differ about 100 times.

CONCLUSIONS

The adsorption rates of four herbicides of esprocarb, thiobencarb, pretilachlor and simetryn in paddy soil from Niigata, Hyogo and Kumamoto in Japan were investigated. The following conclusions were obtained.

(1) It was found that there were two different processes of adsorption for most of the tested systems of herbicide and soil. Namely, part of adsorption occurred quickly within about 30 min of the beginning, then reached the equilibrium slowly after that.

(2) The fast adsorption ratios α were consistently independent of the initial concentration and the constant for each tested system of herbicide and soil.

(3) The adsorption rate in the mixing vessel could be analyzed by equation (6) which was introduced from the first adsorption ratio α and the approximated Boyd equation for slow adsorption.

(4) The values of α were in the range from 0.19 to 1.0. Esprocarb and simetryn had large α for two soils, thiobencarb had α *ca.* 0.66 in all the tested soils, and pretilachlor had various α in the soils.

(5) There was no general tendency for the relationships between the values of α and the various properties of soil including the clay contents and the organic carbon contents, and the fast adsorption of herbicides is not found at the outer site or at the organic substances in the soils. Any correlation of α with the values of P_{ow} and solubilities in water of the herbicides was not recognized.

(6) The adsorption rate parameters of D_i'/r^2 for slow adsorption were in the range of 3.4×10^{-7} to 7.3×10^{-7}/sec when the soil were dispersed into their composing small particles. Any correlation of D_i'/r^2 with the various properties of the soil and herbicide was not found.

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要　　約

除草剤の水田土壌への吸着速度式

岐部香織，高橋　亮，亀屋隆志，浦野紘平

水田除草剤の環境負荷や殺草効果に影響を与える土壌への吸着特性を知るため，4種の除草剤エスプロカルブ，ベンチオカーブ，プレチラクロールおよびシメトリンを用いて，新潟，兵庫，熊本の3種の水田土壌に対する吸着速度を測定した．実験した全ての系で吸着速度が2段階になることを見いだし，平衡吸着量に対する速く吸着する割合αが除草剤濃度によらないことを示した．この結果とBoyd'式の近似式から，2段階の吸着速度式を提案してその適用性を確かめた．早い吸着の割合αが0.19から1.0で土壌と除草剤との組み合わせによって大きく異なるが，供試した土壌や除草剤の物理化学的性状との相関が見いだせなかった．また，遅い吸着の速度パラメータD_i'/r^2は3.4×10^{-7}/secから7.3×10^{-7}/secの範囲であり，土壌や除草剤の種類による差は小さかった．