Adsorption of Pesticides and Their Biodegraded Products on Clay Minerals and Soils

Yuichi Fushiwaki*,[a] and Kohei Urano[b]

[a]*Kanagawa Prefectural Public Health Laboratory, 1–1–1 Nakao, Asahi-ku, Yokohama 241–0815, Japan and* [b]*Yokohama National University, 79–5 Tokiwadai, Hodogaya-ku, Yokohama 240–8501, Japan*

(Received April 19, 2001; Accepted May 16, 2001)

Adsorption isotherms of 10 pesticides and their biodegradation intermediates on clay minerals and soils were investigated to predict the fate of pesticides in the environment. The adsorption isotherms were expressed by the Freundlich isotherm equation. Pentachloronitrobenzene, 2,4,6-trichlorophenyl-4′-nitrophenylether, and various intermediates were highly adsorbed on soils, although isoprothiolane was only slightly adsorbed. The adsorbabilities of pesticides on ando soil, gray lowland soil, and montmorillonite were higher than those on allophene and kaolinite. These results can be used to study the fate of pesticides.

Key words —— adsorption, soil, clay mineral, pesticide

INTRODUCTION

Since most pesticides are used in open environments such as paddy and ploughed fields, survey reports have shown that pesticide residues remain in river water and sediment in Japan.[1] In an intensive farming area where large quantities of pesticides are sprayed, the residues of pesticides and their intermediates in river water were observed throughout the year.[2] Pesticides in river water are biodegraded by microorganisms, although some are adsorbed on suspended solids and accumulate in sediment. We previously reported earlier that pentachloronitrobenzene and its biodegraded intermediates remained in soil over the long term in plough fields.[2] Adsorption on soil is an important physicochemical characteristic governing the fate of pesticides in the environment. Sabljic attempted to predict soil sorption coefficients of organic pollutants from 1-octanol/water partition coefficients.[3] The soil sorption constant and soil organic matter were used as parameters in models to estimate the environmental mobility and fate of pesticides.[4–6] In this study, we attempted to compare the difference in adsorption on a variety of soils and clay minerals as elements of soil with adsorption isotherms.

*To whom correspondence should be addressed: Kanagawa Prefectural Public Health Laboratory, 1–1–1 Nakao, Asahi-ku, Yokohama 241–0815, Japan. Tel.: +81-45-363-1030; Fax: +81-45-363-1037; E-mail: yuichi.fushiwaki@nifty.ne.jp

MATERIALS AND METHODS

Pesticides and Soils —— Pesticides and their biodegraded intermediates were used in this study (Table 1). These pesticides of reagent grade were dissolved in acetone or alcohol, and the resulting solutions were added to pure water for the adsorption tests. Three types of soil sampled in Kanagawa prefecture and five types of clay mineral obtained in Japan were used in this study. These soils and clay minerals are common in Japan. Their properties were measured after drying at 110°C for 4 hr (Tables 2 and 3). Organic carbons were measured using a CHN analyzer (Carlo Erba Instruments model EA 1108). The cation-exchange capacities were obtained by the Schollenberger method. The method used to determine the adsorption isotherms of methanol vapor was applied to obtain the surface area.[7]

Determination of Adsorption Isotherms —— The batchwise adsorption method was applied to obtain the adsorption isotherms. Fixed amounts of the clay minerals or soil were added to aqueous solutions (100 ml) containing 0.02–0.4 mg/l of pesticide in a stoppered 300 ml flask. The flask was shaken at 25 ± 0.5°C for 24 hr. After attaining equilibrium, the mixtures were measured by gas chromatograph after separation of the supernatant. The equilibrium concentration and adsorbed pesticide amount were calculated.

RESULTS AND DISCUSSION

Since the logarithmic plots of the adsorbed pesticide amount against the equilibrium concentrations are approximately linear, the adsorption isotherms can be expressed by the Freundlich equation, $Q=kC^{1/n}$, where Q is the adsorbed amount of pesticide (μg/kg), C is the equilibrium concentration (μg/l), and k and n are the experimental parameters that depend on the system of adsorbent and adsorbate.[8] For example, the adsorption isotherms of CNP

Table 1. Pesticides and Intermediates

Pesticide	Abbreviation	Molecular formula	Solubility in water (mg/l)
Pentachloronitrobenzene	PCNB	$C_6Cl_5NO_2$	0.44
Pentachloroaniline	PCA	$C_6Cl_5NH_2$	—
Pentachlorothioanisole	PCTA	$C_6Cl_5SCH_3$	—
Pentachlorobenzene	PCB	C_6Cl_5H	—
2,4,6-Trichlorophenyl-4′-nitrophenylether	CNP	$C_6H_2Cl_3OC_6H_4NO_2$	0.25
2,4,6-Trichlorophenyl-4′-aminophenylether	CNP-NH_2	$C_6H_2Cl_3OC_6H_4NH_2$	2.0
Chlorothalonil	TPN	$C_6Cl_4(CN)_2$	0.6
Isoprothiolane		$C_2H_4S_2C_2$ $[COOCH(CH_3)_2]_2$	48
Oxadiazon		$(CH_3)_2CHOC_6H_2Cl_2N_2C_2O_2C(CH_3)_3$	0.7
Tolclofosmethyl		$(CH_3O)_2PSOC_6H_2Cl_2CH_3$	0.35

Table 2. Properties of Soil Samples

Symbol	Name	Organic carbon (%)	Surface area (m^2/g)	Cation-exchange capacity (meq/100 g)	Source
A	Ando soil	5.2	120	29.1	Kanagawa, Japan
B	Gray lowland soil	1.4	36	24.2	Kanagawa, Japan
C	Light ando soil	1.1	27	28.8	Kanagawa, Japan

Table 3. Properties of Clay Mineral Samples

Symbol	Name	Surface area (m^2/g)	Cation-exchange capacity (meq/100 g)	Source
D	Montmorillonite	323	105	Yamagata, Japan
E	Na-Bentonite	171	55.6	Yamagata, Japan
F	Ca-Bentonite	372	83.1	Miyagi, Japan
G	Allophane	271	45.0	Tochigi, Japan
H	Kaolinite	29	4.6	Kagoshima, Japan

are shown in Fig. 1 as Freundlich isotherm expressions. The values of k and n for all the systems are listed in Table 4.

The values of n were generally close to 1 with the exception of CNP–NH_2. The following characteristics were noted. The values of n for oxadiazon, tolclofosmethyl, and CNP were about 1.0 ± 0.1 for soils and clay minerals. The adsorption isotherms could be expressed as Henry equations. The values of n for PCB, chlorothalonil, and isoprothiolane were slightly greater than 1. Furthermore, the values of n for CNP–NH_2 were about 2. Therefore the adsorbabilities of CNP–NH_2 were high in a wide range of pesticide concentrations. The values of n for soils were larger than for clay minerals in this study.

The adsorption capacities of the pesticides on the clay minerals and soils were found to be in the following order: PCTA > PCB > CNP–NH_2 > CNP ≈ PCA > PCNB > chlorothalonil > tolclofosmethy > oxadiazon > isoprothiolane except on allophane and kaolinite. The values of k for allophane and kaolinite were fairly low without PCTA and CNP–NH_2. For CNP, PCNB, and chlorothalonil, the adsorption isotherms were similar to those obtained by Kawamoto and Urano.[9,10]

The values of k for PCTA were the largest and those for PCB were larger than those for the other pesticides. The values of k for chlorothalonil, isoprothiolane, oxadiazon, and tolclofosmethyl were small. The values for isoprothiolane, which is more water soluble than the other pesticides, were the lowest. Sharom *et al.* pointed out that the adsorption of pesticides in soils is dependent on their solubility in water.[11] The results of our study support those previous results.[11] Isoprothiolane, which has low adsorbability, was detected in many pond water and wastewater samples at golf courses.[12] The mobility of pesticides from soil to water was observed to change inversely with the extent of adsorption. Therefore isoprothiolane is likely to flow into the

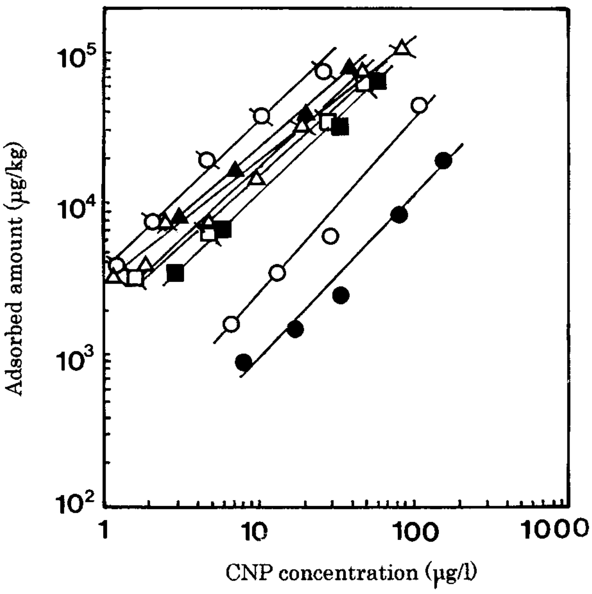

Fig. 1. Adsorption Isotherms of CNP
▲: Na-bentonite; ■: Ca-bentonite; △: montmorillonite; ○: allophane; ●: kaolinite; ˋ△: gray lowland soil; ˋ○: ando soil; ˋ□: light ando soil.

water environment. The values of k for soils were greater than those for clay minerals. In clay minerals, large values of k were obtained for montmorillonite, Ca-bentonite, and Na-bentonite. It was expected that these clay minerals of the montmorillonite group with larger molecular structure could adsorb organic compounds in each of the layers.

Bailey and White studied the factors influencing adsorption of pesticides in soil[13] and reported that montmorillonite has considerable adsorption capacity because of its large surface area. The results of Bailey and White agree with those of the present study. Furthermore, the adsorbabilities on Na-bentonite were higher than on the other clay minerals except for CNP–NH_2. This suggests that the adsorbabilities of pesticides on Na-bentonite are different from those on other minerals. The reason may be that the surface area of Na-bentonite, which characteristically undergoes large swelling, is increased to 300–450 m^2/g in the wet state.[14]

In general, the amount of pesticides adsorbed on soils has been reported to be related to the organic carbon contents of soils.[15] However, in this study, the adsorption of pesticides on soils was not clearly related to the organic carbon contents. Shimizu reported that there is no relation between adsorption and organic carbon in soil in the case of low organic content, and organic chemicals were also adsorbed on inorganic matter in soil.[16] Therefore the differences in the adsorbed amounts may also be attributed to inorganic matter.

Kanazawa reported that significant correlations were found between the soil sorption constants of pesticides and their physicochemical properties.[15] Moreover, adsorption isotherms were fitted to the Freundlich equation, and the values of k and n for CNP and oxadiazon were similar to those in our study.[15]

Protonation to the amino group in CNP–NH_2 and PCA may cause ionic attraction to the negative charge of soil particles. Therefore the soils and clay minerals had higher adsorption capacities for CNP–NH_2 and PCA than for CNP and PCNB because of their high cation-exchange capacities.

Intermediates such as PCA, PCTA, and PCB, which are the principal biodegradation products of PCNB and CNP–NH_2, which is formed by the biodegradation of CNP under anaerobic conditions,[17] were adsorbed more readily than intermediates of PCNB and CNP in this study. The Kobusawa River

Table 4. Values of k and n for the Freundlich Equation

Pesticide	$k(1^{1/n}\ \mu g^{1-1/n}\cdot kg^{-1})$								n							
	A	B	C	D	E	F	G	H	A	B	C	D	E	F	G	H
PCNB	2000	1500	300	800	1000	200	40	20	1.0	1.0	0.91	0.91	0.83	0.71	0.83	0.86
PCA	4000	1200	600	300	420	1000	10	4	1.2	1.0	0.91	0.83	0.71	0.83	0.63	0.56
PCTA	30000	20000	9000	20000	42000	—	7000	4400	1.0	0.91	1.2	0.67	0.87	—	0.71	0.80
PCB	15000	10000	4000	8000	12000	9000	80	40	1.7	1.7	1.2	1.2	1.1	1.2	0.74	0.74
CNP	3200	3000	1700	1700	3000	1000	180	80	1.0	1.2	1.0	1.1	1.0	1.0	0.83	0.95
CNP-NH_2	6500	6000	1700	2000	2000	3000	2000	4000	2.0	2.5	2.2	1.8	1.8	2.0	2.0	2.0
Chlorothalonil	700	500	300	1000	2000	1000	70	110	1.4	1.5	1.8	1.4	1.4	1.6	1.3	1.3
Isoprothiolane	40	50	10	70	—	—	60	10	1.2	1.4	1.3	1.2	—	—	1.3	1.1
Oxadiazon	150	120	100	300	—	—	180	80	0.9	0.9	1.0	0.90	—	—	1.1	1.1
Tolclofosmethyl	300	300	50	150	—	—	50	20	1.0	1.1	1.1	0.91	—	—	0.83	0.91

A: ando soil, B: gray lowland soil, C: light ando soil, D: montmorillonite, E: Na-bentonite, F: Ca-bentonite, G: allophane, H: kaolinite.

in Gunma, Japan, contains high concentrations of PCNB, PCA, and PCTA in its sediments.[2)] Similarly, concentrations of CNP and $CNP–NH_2$ are high in the sediments of Lake Kasumigaura.[18)] The results of our study also show that PCNB, CNP, and their intermediates are easily adsorbed on river and lake sediments and suspended solids. These results may be useful in the study of the fate of pesticides.

REFERENCES

1) Fushiwaki, Y. and Urano, K. (1992) Present status and problems for environmental pollution by pesticides. *J. Water Waste Water*, **34**, 1003–1014.
2) Fushiwaki, Y., Tase, N., Saeki, A. and Urano, K. (1990) Pollution by the fungicide pentachloronitrobenzene in an intensive farming area in Japan. *Sci. Total Environ.*, **92**, 55–67.
3) Sabljic, A. (1987) On the prediction of soil sorption coefficients of organic pollutants from molecular structure: Application of molecular topology model. *Environ. Sci. Technol.* **21**, 358–366.
4) McCall, P. J., Laskowski, D. A., Swann, R. L. and Dishburger, H. J. (1983) Estimation of environmental partitioning of organic chemicals in model ecosystems. *Residue Rev.*, **85**, 231–244.
5) Pussemier, L., De Borger, R., Cloos, P. and Van Bladel, R. (1989) Relation between the molecular structure and the adsorption of arylcarbamate, phenylurea and anilide pesticides in soil and model organic adsorbent. *Chemosphere*, **18**, 1871–1882.
6) Bintein, S. and Deviller, J. (1994) QSAR for organic chemical sorption in soils and sediments. *Chemosphere*, **28**, 1171–1188.
7) Urano, K. (1975) Theories apparatuses and problems for determination methods of pore size distributions of porous materials. *Surface* (Japanese), **13**, 588–592, 650–656, 738–745.
8) Urano, K., Koichi, Y. and Nakazawa, Y. (1981) Equilibria for adsorption of organic compounds on activated carbons in aqueous solutions: Modified Freundlich isotherm equation and adsorption potentials of organic compounds. *J. Colloid Interface Sci.*, **81**, 477–485.
9) Kawamoto, K. and Urano, K. (1989) Parameters for predicting fate of organochlorine pesticides in the environment (II) Adsorption constant to soil. *Chemosphere*, **19**, 1223–1231.
10) Kawamoto, K. and Urano, K. (1991) Prediction of environmental fate of organochlorine pesticides in a specific area. *Nippon Kagaku Kaishi*, **1991**, 497–505.
11) Sharom, M. S., Miles, J. R. W., Harris, C. R. and McEwen, F. L. (1980) Pesticide of 12 insecticides in water. *Water Res.*, **14**, 1089–1093.
12) Fushiwaki, Y., Hamamura, T., Hasegawa, A. and Urano, K. (1993) Environmental pollution by pesticides from golf courses in Kanagawa prefecture. *Jpn. J. Toxicol. Environ. Health*, **39**, 543–548.
13) Bailey, G. W. and White, J. L. (1970) Factors influencing the adsorption, desorption and movement of pesticides in soil. *Residue Rev.*, **32**, 29–92.
14) Zhao, X., Urano, K. and Ogasawara, S. (1989) Characteristics of clay minerals of montmorillonites in the wet state. *Nippon Kagaku Kaishi*, **1989**, 209–215.
15) Kanazawa, J. (1989) Relationship between the soil sorption constants for pesticides and their physicochemical properties. *Environ. Toxicol. Chem.*, **8**, 477–484.
16) Shimizu, Y. (1990) Sorption of organic pollutants in aquatic environments: The effects of solid composition. Ph. D. Dissertation, University of Texas at Austin.
17) Fushiwaki, Y. and Urano, K. (1988) Biodegradation test of herbicide CNP in river water and sediment using the modified river die away method. *Water Res.*, **22**, 1137–1141.
18) Ono, H. and Nakanishi, J. (1987) Herbicide, CNP contamination in the Lake Kasumigaura basin. *Water Res.*, **21**, 669–674.