Adsorptive Behavior of [^3H] 2,3,7,8-TeCDD on Seven Japanese Soils using a Batch Equilibrium Method

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Summary

The adsorption behavior of [^3H] 2,3,7,8-TeCDD from water on seven Japanese soils has been evaluated by a batch equilibrium experiment. The experimental conditions of the soil/solution ratio and the equilibrium time were optimized to be 1 : 5000 (50 mg/250 ml) and 72 hours, respectively. The Freundlich adsorption isotherm experiment was conducted at four initial concentrations ranging from 0.005 to 0.06 $\mu\text{g}/\ell$ in the aqueous phase. The adsorption isotherms followed the Freundlich equation with good correlation coefficients. The Freundlich exponents ($1/n$) were close to one. The Freundlich adsorption coefficients (K_F^{ads}) ranged from 9,887 to 97,248. The organic-carbon-normalized Freundlich adsorption coefficients ($\log K_{\text{oc}}^{\text{ads}}$) ranged from 5.58 to 6.77. No positive relation was found between soil parameters (such as organic carbon content, clay content and cation exchange capacity) and adsorption parameters.

Key words: soil adsorption, 2,3,7,8-TeCDD, Freundlich isotherm, batch equilibrium method

INTRODUCTION

An adsorption distribution coefficient is one of the most important parameters for evaluation of the migratory tendency of organic chemicals¹⁾. Many researchers have reported the sorptive behavior of dioxin congeners²⁻⁷⁾. However, most of these values were estimated by the chemical structure or a physical-chemical property, because of the test conditional constraint due to their low water solubility⁵⁻⁷⁾. Therefore, the experimental results for the adsorption parameters of 2,3,7,8-TeCDD were few^{3,4)}. The purpose of this study was to determine the adsorption parameters of [^3H] 2,3,7,8-TeCDD with seven Japanese soils by the batch equilibrium experiments of the OECD Guidelines for Testing of Chemicals¹⁾.

MATERIALS AND METHODS

Test soil

Seven representative soils from Japanese agricultural fields were collected from Ibaraki (*typic hapludands* soil), Chiba (*immature dune* soil), Saitama-1 (*aquic dystic entrudepts* soil), Saitama-2 (*typic dystrodepts* soil), Niigata (*hydraquants* soil), Kumamoto (*typic hapludands* soil), and Miyazaki (*immature dune* soil) and were used in this experiment. The soils were air-dried and sieved through a 2-mm mesh sieve prior to use. The moisture contents of the sieved soils were determined on three aliquots (ca. 5 g) with heating at 100°C for over 12 hours. The test soils were characterized by Palyno Survey Co., Ltd., (Japan) for texture, organic carbon content, clay content, cation exchange capacity (CEC), and main clay mineral. The soil properties used for this experiment are summarized in Table 1.

Table 1 Properties of soils used for sorption isotherm experiments

Soil (Sampling point)	Ibaraki (Ushiku)	Chiba (Nosaka)	Saitama-1 (Kumagaya)	Saitama-2 (Chichibu)	Niigata (Nagaoka)	Kumamoto (Koshi)	Miyazaki (Sadowara)
Soil taxonomy	<i>Typic hapludands</i>	<i>Immature dune soil</i>	<i>Aquic dystic eutrudepts</i>	<i>Typic dystrudepts</i>	<i>Hydraquants</i>	<i>Typic hapludands</i>	<i>Immature dune soil</i>
Texture ^{a)}	Silty clay loam	Sand	Clay loam	Light clay	Light clay	Light clay	Sand
Particle size distribution, %							
Fine sand (2-0.02 mm)	26.2	96.3	47.9	37.4	24.4	24.4	90.1
Silt (0.02-0.002 mm)	50.9	1.7	27.9	24.3	44.5	41.6	5.2
Clay (<0.002 mm)	22.9	2.0	24.2	38.3	31.1	34.0	4.7
Organic carbon content, %	2.25	0.37	1.29	1.42	1.65	7.65	0.96
pH in water	6.8	5.9	5.6	6.7	5.3	6.4	6.2
pH in 0.01 mol/l CaCl ₂	5.6	4.4	4.1	5.1	4.4	5.0	4.6
CEC ^{b)} , cmol(+)/kg	21.4	2.3	9.9	14.2	21.5	33.4	6.4
Moisture content, %	14.1	0.7	2.2	4.1	0.7	14.2	2.9
Main clay mineral	allophane, vermiculite	chlorite	illite, chlorite	kaolinite, chlorite	montmorillonite, kaolinite	allophane	allophane, halloysite

^{a)} Classification according to the International Soil Survey Conference.

^{b)} Cation exchange capacity.

Reagents

A standard stock solution of 1,6-³H-labeled 2,3,7,8-TeCDD in toluene was purchased from ChemSyn Laboratories (USA). The specific radioactivity was 34.7 Ci/mmol (107.8 μ Ci/ μ g), and the radiochemical purities were 94 % according to analysis by high performance liquid chromatography with liquid scintillation counting (HPLC-LSC). The analysis was conducted with a LC-6A HPLC system (Shimadzu Co.,) equipped with an LC-5100 (Aloka Co.,). The standard stock solution was diluted with methanol to 200 ml total. This working standard solution was stored in a refrigerator prior to use.

Water was generated using a Milli-Q purifier system obtained from Millipore (USA). All organic solvents were of pesticide residue, PCB or HPLC analysis grade. All other reagents were of reagent grade. All solvents and reagents used in this study were purchased from Kanto Chemical Co., Inc., (Japan).

Pre-equilibration of test soils

All the experiments were carried out under in the dark at 25 °C in duplicate. Fifty milligrams (as oven-dried mass) of the soils were pre-equilibrated with 250-ml of 0.01 mol/l calcium chloride (CaCl₂) solution in glass vessels. The test vessels were tightly capped, and they were then shaken using a reciprocating shaker (Taitec, NR-80).

Determination of adsorption equilibrium time

An aliquot (50 μ l) of the working standard solution of [³H] 2,3,7,8-TeCDD was added to the pre-equilibrated Ibaraki soil to give a 0.01 μ g/l initial concentration in the aqueous phase. The sample was shaken by using the reciprocating shaker. A part of the aqueous phase was dispensed into a glass centrifuge tube (COREX®); the tube was then tightly capped and centrifuged for 30-min at approximately 10,100×g using an ultracentrifugal separator (H2000A2, Kokusan, Japan) while maintained at 25 °C. To determine the period of the adsorption equilibrium, tritium-radioactivity in the separated supernatants was immediately quantified using a liquid scintillation counter after 5, 10, 24, 48, 72 and 96 hours agitation. A control sample with only the [³H] 2,3,7,8-TeCDD in 0.01 mol/l CaCl₂ solution without soil was simultaneously prepared and analyzed at the same time intervals.

Freundlich adsorption isotherm

The Freundlich isotherm experiment was conducted at the four dose levels ranging in the initial concentration of the aqueous phase from 0.005, 0.01, 0.02 to 0.06 (0.05 for Chiba-soil) μ g/l. Twenty-five, fifty and one-hundred micro-liters of the working standard solutions were added to the pre-equilibrated test soils to give 0.005, 0.01 and 0.02 μ g/l initial concentrations, respectively. The highest initial concentration at 0.06 μ g/l was carried out by repeating 100 μ l injections of the working standard solution three times

at 24-hour intervals, except for the Chiba soil in which the final injected volume was reduced to 50 $\mu\ell$ to adjust the concentration to 0.05 $\mu\text{g}/\ell$. The radioactivity in the supernatants was quantified after 72 hours agitation. In the case where the repeated application procedure was performed, the sample was agitated for a period of 72 hours after the last application. The other test conditions and procedures were the same as in the previous section.

Radioassay

Tritium radioactivity was determined for portions of the clear supernatants using a liquid scintillation counter with a scintillation cocktail (Atomlight™, Packard Inc., USA) in duplicate. The mean values of two measurements for 2 min were calculated for the estimation. The detection limit of LSC analysis was 62 dpm which was corrected twice for representative background levels (22 dpm) of radioactivity in the soil-solution suspension.

Calculation of adsorption parameters

The percentage of adsorption (A) was calculated from the concentrations of [^3H] 2,3,7,8-TeCDD in the aqueous phase (C_{aq}) using the following equation:

$$A = m_s/m_o \times 100 = (m_o - C_{aq} \times V_o)/(C_o \times V_o) \times 100$$

where m_s is the mass of [^3H] 2,3,7,8-TeCDD adsorbed on the soil (μg), m_o is the initial mass of [^3H] 2,3,7,8-TeCDD in the test system (μg), C_o is the initial concentration in the aqueous phase ($\mu\text{g}/\text{m}\ell$), and V_o is the initial volume of the test solution in contact with the soil ($\text{m}\ell$).

The distribution coefficient for adsorption (K_d) was calculated using the following equation:

$$K_d = C_s/C_{aq} = (m_s/m_{aq}) \times (V_o/m_{\text{Soil}})$$

where C_s is the content of [^3H] 2,3,7,8-TeCDD adsorbed on the soil ($\mu\text{g}/\text{g}$), m_{aq} is the mass of [^3H] 2,3,7,8-TeCDD in the aqueous phase (μg), and m_{Soil} is the quantity of the soil phase, expressed as dry mass of the soil (g).

The adsorption isotherm was prepared on $\log C_{aq}$ versus $\log C_s$. The values of the Freundlich adsorption coefficient (K_F^{ads}) and the Freundlich exponent ($1/n$) were calculated by a regression analysis based on the Freundlich equation:

$$\log C_s = \log K_F^{ads} + 1/n \log C_{aq}$$

The organic-carbon-normalized Freundlich adsorption coefficient (K_{Foc}^{ads}) was also calculated using the following equation:

$$K_{Foc}^{ads} = K_F^{ads} / f_{oc} \times 100$$

RESULTS AND DISCUSSION

Optimization of test conditions

In general, it is recommended that the test vessel for the adsorption experiment be fitted directly in a centrifuge apparatus in order to minimize handling and transfer errors. In addition, a large volume vessel is necessary in the adsorption experiment for 2,3,7,8-TeCDD due to its low water solubility. A Teflon-coated stainless-steel centrifuge tube (500-m ℓ) had been preliminarily tested for this experiment. However, most of the [^3H] 2,3,7,8-TeCDD had been adsorbed on the surface of the test vessels (data not shown). Therefore, a 500-m ℓ glass vessel and a 25-m ℓ glass centrifuge tube were used for the agitation and centrifugation steps, respectively. The centrifuge condition applied in this experiment can remove soil particles ranging in diameter from 0.095 to 0.024 μm , where the soil densities are assumed to be in the range of 1.2 to 4 g/cm^3 .

The soil/solution ratio for this experiment was optimized to 1 : 5000 (w/v) based on a preliminary test using the Ibaraki soil (data not shown), which is referred to the reported data ($\log K_{Foc}^{ads} = 6.6$)³⁰.

Adsorption equilibrium time

The determination of the adsorption equilibrium time was conducted at 0.01 $\mu\text{g}/\ell$ initial concentration in the aqueous phase for the Ibaraki soil. The results of the time course determination are plotted in Figure 1. The adsorption equilibrium of [^3H] 2,3,7,8-TeCDD is immediately attained with in 48 or 78 hours after initiation. A simple comparison of the adsorption equilibrium time is difficult, because it was influenced by the experimental test conditions. For example, R.W. Walters and A. Guiseppi-Elie³⁰ have evaluated the adsorption equilibrium time of ^{14}C -labeled 2,3,7,8-TeCDD for soils from water/methanol mixtures to be between less than a day and 30 days, using a batch equilibrium method. D.C. Girvin and Al J. Scott²⁹ have evaluated the adsorption equilibrium time of PCBs to be be-

tween 3 and 10 months, using a gas-purge method. The adsorption equilibration time in a subsequent isotherm experiment was conducted at 72 hours for all the test soils.

As shown in Figure 1, approximately 40 % of [^3H] 2,3,7,8-TeCDD in the control samples had been adsorbed on the surface of the test vessel. However, the adsorption loss on the surface of the glass vessel was smaller than the loss on the Teflon-coated stainless-steel vessel, as stated above. In addition to that, the presence of soil will generally reduce this adsorption phenomenon. Thus, it was assumed that this problem does not significantly influence the determination of the adsorption parameters of [^3H] 2,3,7,8-TeCDD.

Application of [^3H] 2,3,7,8-TeCDD

Generally, the dose levels of a chemical for an adsorption experiment are conducted at concentrations below half of the water solubility. In the case of 2,3,7,8-TeCDD, the highest initial concentration was planned to be at $0.020\ \mu\text{g}/\ell$, almost equal to half of the water

solubility. On the other hand, the lowest initial concentration was set up based on the adsorption ability and the detection limit of test chemicals. In this study, the lowest initial concentration was set at $0.005\ \mu\text{g}/\ell$ based on the detection limit of [^3H] 2,3,7,8-TeCDD and the background radioactivity in the supernatants with soils. However, the concentration range of the adsorption isotherm is very narrow. Therefore, we partially solved this problem by repeated applications three times at half of the water solubility, when the concentration of [^3H] 2,3,7,8-TeCDD in the aqueous phase was maintained at less than its water solubility. For the adsorption isotherm experiment in this study, the initial concentrations in the aqueous phase (0.005 – $0.060\ \mu\text{g}/\ell$) covered one order of magnitude. The application of [^3H] 2,3,7,8-TeCDD for the highest initial concentration was performed on sequencing $100\text{-}\mu\ell$ injections of the working standard solution three times at 24-hour intervals. However, the initial concentration for the Chiba soil with the lowest adsorption nature was conducted at $0.05\ \mu\text{g}/\ell$, because there was a pos-

Fig. 1 Time course of the concentrations of [^3H] 2,3,7,8-TeCDD in adsorption supernatant obtained from the Ibaraki soil

sibility that the concentration exceeded the water solubility of 2,3,7,8-TeCDD. The concentrations of methanol in the aqueous phase as a solubilizing co-solvent were below 0.12 %.

Adsorptive behavior of [^3H] 2,3,7,8-TeCDD

The adsorption parameters for each soil, such as the percentages of adsorption (A), the distribution coefficients (K_d) and the Freundlich isotherm parameters are summarized in Table 2. The percentages of adsorption ranged from 64.8 % for the Chiba soil to 93.9 % for the Niigata soil. The K_d for Ibaraki soil, the Chiba soil, the Saitama soil-1, the Saitama soil-2, the Niigata soil, the Kumamoto soil, and the Miyazaki soil were 27,488, 9,311, 47,047, 31,243, 79,965, 56,012 and 15,717, respectively. The K_d obtained from two kinds of immature dune soils (the Chiba soil and the Miyazaki soil) were relatively low, as compared to the values of other soil types.

The Freundlich adsorption isotherms for seven soils are plotted in Figure 2. The coefficients of correlation (γ^2) of the isotherms were better than 0.994 for all of the test soils. This result indicates that the sorption of [^3H] 2,3,7,8-TeCDD is possible as described by the Freundlich equation. The Freundlich isotherm slope is close to one, as the exponent ($1/n$) of regression ranged from 0.952 to 1.055. Therefore, the K_F^{ads} approximated by K_d , the ratio of adsorbed [^3H] 2,3,7,8-TeCDD to the concentration in the equilibrium solu-

tion. The K_F^{ads} ranged from 9,887 for the Saitama soil 1 to 97,248 for the Niigata soil. The organic-carbon-normalized Freundlich adsorption coefficients ($\log K_{Foc}^{ads}$) ranged from 5.58 for the Kumamoto soil to 6.77 for the Niigata soil.

Many researchers have reported the soil adsorption of PCDD/Fs and/or PCBs²⁻⁷⁾, although several of them vary. The variation in them is probably influenced by the test conditional constraint due to the low water solubility. For example, most of these values are estimated from the chemical structure or a physical-chemical property⁵⁻⁷⁾, or calculated by extrapolation from a specific experiment using a soil suspension with a water/methanol mixture^{3,4)}. The experimental results of this study are in agreement with these reported values.

In addition, the measured $\log K_{Foc}^{ads}$ in this experiment are one order lower than the organic-carbon-normalized desorption coefficients ($\log K_{oc}^{des}$) in the range of 6.88 to 7.58, which were obtained from actual soils contaminated with dioxin congeners and are described elsewhere in this journal.

Seven soils covering wide texture types were selected for this study in order to analyze the relationship between soil properties and the behavior of 2,3,7,8-TeCDD. As shown in Table 1, the organic carbon contents ranged from 0.37 to 7.65 %, the clay contents ranged from 2.0 to 38.3 % and the cation exchange capacities (CEC) of the soils ranged from 2.3

Table 2 [^3H] 2,3,7,8-TeCDD adsorption parameters for Freundlich model, the percentages of adsorption (A) and the distribution coefficients for adsorption (K_d)

Soil	A^a	K_d^a	$\log C_S = \log K_F^{ads} + 1/n \log C_{aq}$			$\log K_{Foc}^{ads, b)}$
			K_F^{ads}	$1/n$	R^2	
Ibaraki	84.5	27,488	21,994	0.983	0.997	5.99
Chiba	64.8	9,311	18,043	1.055	0.994	6.69
Saitama-1	90.3	47,047	24,757	0.953	0.999	6.28
Saitama-2	86.1	31,243	9,887	0.912	0.998	5.84
Niigata	93.9	79,965	97,248	1.016	0.997	6.77
Kumamoto	91.7	56,012	28,962	0.952	0.996	5.58
Miyazaki	75.8	15,717	13,155	0.986	0.998	6.14

^{a)} Mean values for concentrations of 0.005 to 0.06 $\mu\text{g}/\ell$.

^{b)} The organic-carbon-normalized Freundlich adsorption coefficients.

Fig. 2 Freundlich adsorption isotherms of $[^3\text{H}]$ 2,3,7,8-TeCDD by seven Japanese soils
A dotted line expresses the water solubility of $[^3\text{H}]$ 2,3,7,8-TeCDD at 2×10^{-5} mg/l.
(72 hours agitation, 50 mg soil/250 ml CaCl_2 aq.)

to 33.4 cmol (+). Figure 3 shows the relationship of the organic carbon contents, CEC and clay contents of the soils with the K_d of $[^3\text{H}]$ 2,3,7,8-TeCDD. There was no significant correlation with soil parameters and adsorption parameters. The K_d of the hydraquants type soil for the Niigata soil was relatively high in comparison with other soils.

CONCLUSIONS

The lowest K_d within the seven Japanese soils in this investigation was ca. 9,000 obtained from the Chiba soil (*immature dune* soil). On the contrary, the highest was ca. 80,000 obtained from the Niigata soil (*hydraquants* soil). Organic-carbon-normalized Freundlich adsorption coefficients ($\log K_{Foc}^{ads}$) ranged from 5.58 to 6.77. The $\log K_{Foc}^{ads}$ obtained from two kinds of *typic hapludands* soils were relatively low compared with the values from other soil types. There was no significant correlation with soil parameters (such as organic carbon contents, clay contents and CEC) and adsorption parameters.

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Fig. 3 Relationship of organic carbon contents (A), CECs (B) and clay contents (C) of seven soils with the K_d of [^3H] 2,3,7,8-TeCDD

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