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Journal of Agricultural and Food Chemistry, 2016, 64, 4478~4486 より
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Effect of Time-Dependent Sorption on the Dissipation of Water-Extractable Pesticides in Soils

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Effect of Time-Dependent Sorption on the Dissipation of Water-Extractable Pesticides in Soils

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S Supporting Information

ABSTRACT: The dissipation behavior of water-extractable pesticides in soils is important when assessing the phytoavailability of pesticides in soils. This process is less understood than pesticide extraction with organic solvents. To elucidate the dissipation behavior of water-extractable pesticides in soils, we conducted an incubation study using 27 pesticides and five Japanese soils. The rate of decrease of the level of pesticides in water extracts was faster in soils than that of total extracts (water extracts and acetone extracts). This suggests that time-dependent sorption contributed to the difference in the dissipation between the pesticides in water and total extracts from soils. Increased apparent sorption coefficients ($K_{d,app}$) with time were positively and significantly correlated with $K_{d,app}$ values of a 0 day incubation [$K_{d,app}(t_0)$]. This empirical relationship suggests that $K_{d,app}(t_0)$ values can predict the time-dependent increase in $K_{d,app}$ and the dissipation of water-extractable pesticides in soils.

KEYWORDS: pesticides, soil, fate, aging, time-dependent sorption, water extraction, phytoavailability

INTRODUCTION

Recently in Japan, some agricultural chemicals that had been applied to previously grown crops and then remained in the soil were detected in succeeding crops. Selling or distributing crops in Japan that contain pesticides above their maximal residue limits (MRLs), or a concentration of 0.01 mg/kg if the MRL has not been established, is prohibited.¹ Thus, these farmers suffer economic loss. When newly developed pesticides are registered in Japan, soil dissipation studies in two fields having different soil types are required.² These studies must be performed to assess the risk of contamination succeeding crops by pesticide residue in soils; that is, studies of residues in succeeding crops² are required only if the half-lives of pesticides in the soil are more than 100 days.

In soil dissipation studies, the extraction of pesticides from soils is conducted using organic solvents such as acetone. However, the extractability of organic solvents is too high to assess the phytoavailability of residual pesticides in soil,³ i.e., the organic solvent extracts soil-sorbed pesticides, which are not taken up by the plant. Therefore, to estimate the plant uptake of residual pesticides in soils, the concentrations of phytoavailable pesticides in soils should be measured. Our previous study indicated that the concentrations of pesticides such as clothianidin, thiacloprid, procymidone, and tetraconazole in leafy vegetables cultivated in four different soils containing the pesticide residues were positively and significantly correlated with the concentrations of water-extractable pesticides rather than total extractable pesticides (water extracts and acetone extracts) in these soils.⁴ This result implies that the residual levels of pesticides in crops are estimated using the concentrations of water extracts from soils. In addition, the study showed that the coefficients of determination (R^2) calculated using the concentrations of water extracts from soils at harvest were higher than those at sowing. Therefore,

assessing the dissipation of water-extractable pesticides in soils and predicting the concentration of the aqueous soil extracts at harvesting time are important for estimating the residue levels in crops before harvest, preferably before sowing, and for preventing the production and distribution of pesticide-contaminated crops. On the other hand, the water-extractable concentrations of pesticides can be calculated using the pesticide concentrations extracted with an organic solvent and the soil sorption coefficient (K_d), which describes the distribution of pesticides between soil and water. Hence, understanding the variability in K_d values is also important for estimating the uptake concentrations of pesticides from soils by crops.

K_d values measured by the batch equilibrium method⁵ are required for four different soils under the Japanese registration system.² The registration data for the soil dissipation study and the soil sorption study may be available for estimating the residual concentrations of water-extractable pesticides in soils and the uptake concentrations in crops. However, it was reported that the K_d values of various pesticides, including insecticides,^{6–9} fungicides,^{10,11} and herbicides,^{9,11–15} increased with aging time. Hence, if the effect of aging on the K_d values is not considered, the concentrations of water-extractable pesticides predicted using the K_d values seem to be higher than the actual values. Many previous studies^{6–8,10,12–15} describing and assessing time-dependent sorption have been conducted on either individual pesticides or several pesticides, and thus, the time-dependent changes in K_d values have not

Received: March 2, 2016

Revised: May 16, 2016

Accepted: May 19, 2016

Published: May 27, 2016

Table 1. Properties of Test Soils

soil	experiment	classification ^a	texture ^b	OC ^c (%)	CEC ^d (cmol(+) kg ⁻¹)	clay (%)	pH (H ₂ O)	EC ^e (mS cm ⁻¹)
LS1 ^f	laboratory	Typic Udipsamments	sand	0.06	3.4	2.4	7.5	0.04
LS2 ^f		Typic Hapludults	light clay	1.02	11.4	39.0	5.3	0.09
LS3 ^f		Typic Endoaquents	silty clay	1.46	18.2	25.3	5.8	0.17
LS4 ^f		Typic Hapludands	loam	5.21	33.8	10.8	5.5	0.15
LS5 ^f		Pachic Melanudands	silty loam	8.65	35.4	1.8	5.8	0.05
FS	field	Typic Hapludands	silty loam	4.93	26.0	7.3	6.3	0.31

^aAccording to U.S. Department of Agriculture Soil Taxonomy.¹⁷ ^bAccording to the International Society of Soil Science.¹⁹ ^cOrganic carbon content. ^dCation exchange capacity. ^eElectrical conductivity. ^fData were obtained from our previous report.²⁰ Soils LS1–LS5 correspond to soils S1, S3, S5, S7, and S8, respectively, in the previous report.

Table 2. Hydrophobicities and Analytical Groups of Test Compounds

compound	CAS Registry No.	pesticide type ^a	substance group	log <i>P</i> _{ow} ^b	log <i>S</i> _w ^c	analytical group ^d	
						laboratory test	field test
dinotefuran	165252-70-0	I	neonicotinoid	-0.549	4.60	A	A
imidacloprid	138261-41-3	I	neonicotinoid	0.570	2.79	A	A
dimethoate	60-51-5	I	organophosphate	0.704	4.60	A	
clothianidin	210880-92-5	I	neonicotinoid	0.905	2.53	A	A
thiacloprid	111988-49-9	I	neonicotinoid	1.26	2.26	A	A
fosthiazate	98886-44-3	I	organophosphate	1.68	3.95	A	A
metalaxyl	57837-19-1	F	phenylamide	1.75	3.92	A	A
ethiprole	181587-01-9	I	phenylpyrazole	1.99	0.964	A	
azoxystrobin	131860-33-8	F	methoxyacrylate	2.50	0.826	C	
methidathion	950-37-8	I	organophosphate	2.57	2.38	A	
fenobucarb	3766-81-2	I	carbamate	2.78	2.62	B	C
boscalid	188425-85-6	F	pyridinecarboxamide	2.96	0.663	B	
flutolanil	66332-96-5	F	phenylbenzamide	3.17	0.904	B	C
procymidone	32809-16-8	F	dicarboximide	3.30	0.391	B	C
fenitrothion	122-14-5	I	organophosphate	3.32	1.28	C	
kresoxim-methyl	143390-89-0	F	oximinoacetate	3.40	0.301	B	
tetraconazole	112281-77-3	F	triazole	3.56	2.19	C	
chloroneb	2675-77-6	F	chlorophenyl	3.58	0.903	B	
diazinon	333-41-5	I	organophosphate	3.69	1.78	C	
propiconazole	60207-90-1	F	triazole	3.72	2.18	C	
fipronil	120068-37-3	I	phenylpyrazole	3.75	0.577	C	
cadusafos	95465-99-9	I	organophosphate	3.85	2.39	B	
diclocymet	139920-32-4	F	carboxamide	3.97	0.805	C	
trifloxystrobin	141517-21-7	F	oximinoacetate	4.50	-0.215	B	
tolclofos-methyl	57018-04-9	F	organophosphate	4.56	-0.150	C	C
tetradifon	116-29-0	I	bridged diphenyl	4.61	-1.11	C	
fenthion	55-38-9	I	organophosphate	4.84	0.623	B	

^aAbbreviations: I, insecticides; F, fungicides. ^bOctanol–water partition coefficient obtained from the Pesticide Properties Database of IUPAC,²¹ except for the *P*_{ow} of diclocymet, which was obtained from ref 22. ^cWater solubility (milligrams per liter) obtained from the Pesticide Properties Database of IUPAC,²¹ except for the *S*_w of ethiprole, which was obtained from ref 22. ^dThe details of analytical methods are described in our previous report.²⁰

been extensively evaluated using various pesticides with different physicochemical properties for a given soil.

Because the soil organic matter is a main sorbent of a nonionic pesticide,¹⁶ it is likely to play an important role in the time-dependent increase in the *K*_d values for nonionic pesticides. However, there is no report on the time-dependent changes in *K*_d values in soils having a wide range of organic carbon (OC) contents. On the other hand, Japan is a typical volcanic country; volcanic ash soil (andisol), which is one of the major upland soils and is also widely distributed in other circum-Pacific regions such as the western coast of the American continents, the Philippine Islands, and New Zealand,¹⁷ contains high OC content. Therefore, Japanese soils have a wide range of OC contents¹⁸ and are useful for

elucidating the relationships between the time-dependent changes in *K*_d values and the OC content.

The aims of this study are to elucidate the dissipation behavior of the concentrations of pesticides in water extracts and total extracts (water extracts and acetone extracts) from soils and the time-dependent changes in the *K*_d values in laboratory experiments using five Japanese soils with different OC contents and 27 pesticides with different physicochemical properties. Furthermore, we attempted to develop an estimation method that can predict the dissipation of the water-extractable pesticides using the initial *K*_d values (i.e., the 0 day values after application of pesticides), based on the results of the laboratory studies, and verify this estimation method in the field.

MATERIALS AND METHODS

Soils and Pesticides. Five typical Japanese agricultural soils with a wide range of OC contents were used in the laboratory studies. Soil samples were air-dried and passed through a 2.0 mm sieve. The soil properties are listed in Table 1. The methods for measuring the reported properties have been described previously.²⁰ The 27 pesticides (chemical purity of >97.0%) were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan), Kanto Chemicals (Tokyo, Japan), and Dr. Ehrenstorfer GmbH (Augsburg, Germany) (Table 2). Pesticides belonging to various chemical groups were chosen on the basis of hydrophobicity, i.e., the range of their octanol–water partition coefficients ($\log P_{ow}$) and water solubility ($\log S_w$). To permit simultaneous analysis, the pesticides were divided into three analytical groups on the basis of the analytical methods described in Pesticide Analysis. Stock solutions (100 $\mu\text{g}/\text{mL}$ each) of the pesticides were prepared in acetone for each group.

Laboratory Incubation. Air-dried soil equivalent to 8 g of dry weight (DW) was placed in a 50 mL glass centrifuge tube. The water content of the soils was adjusted to approximately 60% of water holding capacity (WHC). Duplicate samples were incubated at 25 ± 2 °C in the dark. After a preincubation period of 10 days, 80 μL of an acetone stock solution of each pesticide group was added dropwise to a soil sample in a test tube so that the sample concentration was 1 $\mu\text{g}/\text{g}$ of DW of the initial pesticide concentration. The soil samples were thoroughly mixed using a microspatula, and the openings of the tubes were covered with aluminum foil. The soil samples were incubated in the dark at 25 ± 2 °C for 0, 2, 7, 14, 30, 60, and 120 days. The moisture content was maintained at 50–60% of WHC by adding distilled water once every 10 days. After each incubation period, the soil samples were analyzed using a sequential extraction method using distilled water and acetone.⁴

Sequential Extraction of Soils. Forty milliliters of distilled water was added to the test tubes so that the soil/solution ratio was approximately 1/5. The tubes were agitated on a thermostat shaker (TAITEC, Saitama, Japan) for 24 h at 25 ± 2 °C in the dark. After being shaken, the mixtures were centrifuged at 1200g for 30 min. Fifteen milliliters of supernatant was withdrawn and used to quantify the water-extractable pesticides, and then 20 mL of supernatant was discarded. Subsequently, 30 mL of acetone was added to the remaining sample; the tubes were shaken in a thermostat shaker for 20 min at 25 ± 2 °C and centrifuged at 1200g for 10 min, and then the supernatant was carefully decanted. This extraction procedure was repeated twice. The collected supernatant was evaporated in a rotary evaporator to reduce the volume to <15 mL, which was then used to quantify the acetone-extractable pesticides.

Pesticide Analysis. The aliquots (15 mL) of water extracts and concentrates (<15 mL) of acetone extracts from soils were analyzed using three different methods for each analytical group, as described in our previous report.²⁰ In brief, the aliquots and concentrates were cleaned with a diatomite column (InertSep K-solute 20 mL; GL Sciences, Tokyo, Japan) followed by these solid phase extraction (SPE) cartridges: a PSA column (500 mg; Supelco, Bellefonte, PA), an Accell CM column (500 mg; Waters, Milford, MA), and an ENVI-Carb II/PSA column (500 mg/500 mg; Supelco) for groups A–C, respectively (Table 2). The cleaned samples were analyzed by liquid chromatography and tandem mass spectrometry (LC–MS/MS) for group A and gas chromatography and mass spectrometry (GC–MS) for groups B and C. The LC–MS/MS and GC–MS operating conditions are given in Supporting Information section SI-1. In the case of the high matrix effects of cleaned samples, the quantification of pesticides using GC–MS was performed using matrix-matched standards.²³

The mass fraction of water-extractable pesticides in the soil, C_W (micrograms per gram of DW), was calculated from

$$C_W = C_{aq}(V_{add} + V_{sw})/M_{soil} \quad (1)$$

where C_{aq} (micrograms per milliliter) is the mass concentration of pesticide in the aqueous phase after shaking for 24 h, V_{add} is the volume of distilled water added (milliliters), V_{sw} is the volume of soil

water (milliliters), and M_{soil} is the soil's dry mass (grams). The mass fraction of total extractable pesticides in the soil, C_T (micrograms per gram of DW), was represented as

$$C_T = [C_{aq}(V_{aliq} + V_{disc}) + m_E]/M_{soil} \quad (2)$$

where V_{aliq} is the volume of the aliquot taken from the supernatant (milliliters), V_{disc} is the volume of the discarded supernatant (milliliters), and m_E is the mass of the pesticides extracted by acetone from the remaining sample after V_{aliq} and V_{disc} were removed (micrograms).

Two kinetic models were used to describe the dissipation in C_W and C_T with time: a single-first-order (SFO; eq 3) model and a double-first-order in parallel (DFOP; eq 4) model.²⁴ The DFOP model describes the dissipation as a sum of two first-order dissipation steps each in different parts of the soil compartment. The dissipation parameters were obtained by using the least-squares method with Microsoft Excel Add-In Solver.

$$C(t) = C_0 e^{-kt} \quad (3)$$

$$C(t) = C_0[f e^{-k_1 t} + (1 - f)e^{-k_2 t}] \quad (4)$$

where $C(t)$ is the C_W or C_T value after t days, C_0 is the C_W or C_T value at time zero, k is the rate constant (inverse days), f is the fraction of C_0 applied to the first compartment, and k_1 and k_2 are the rate constants in the first and second compartments, respectively.

For the SFO model, DT_{50} (days), which is the time taken for a 50% decrease in C_W or C_T , was calculated using

$$DT_{50} = \ln 2/k \quad (5)$$

For the DFOP model, the DT_{50} values were calculated by using the goal-seek function in Microsoft Excel.²⁴

The apparent sorption coefficients ($K_{d,app}$, milliliters per gram) after different incubation periods, taking the dissipation of C_T and C_W with time into consideration, were determined using

$$K_{d,app} = C_{sorb}/C_{aq} = (C_T - C_W)/C_{aq} \quad (6)$$

where C_{sorb} is the mass fraction of soil-sorbed pesticides (micrograms per gram of DW).

Pesticide recovery tests were conducted with distilled water and all test soils.²⁰ Samples of distilled water (15 mL) spiked with a pesticide concentration of 1 ng/mL for all group pesticides were analyzed using the methods mentioned above. Each soil (5 g) spiked with 5 and 3 ng/g for group A and groups B and C, respectively, was mixed with 10 mL of distilled water and subsequently extracted three times with 30 mL of acetone for 20 min at 25 ± 2 °C. The acetone extracts were analyzed in a similar way. The mean recovery from the four replicates for group A and five replicates for groups B and C ranged from 73.2 to 117.0% for all compounds; the coefficients of variation (CVs) were $\leq 19.0\%$. The limits of quantification (LOQs) were calculated in accordance with Japanese Industrial Standard (JIS) K 0312.²⁵ The LOQs for all compounds in distilled water and all test soils were in the ranges of 0.14–1.29 ng/mL and 0.23–5.93 ng/g, respectively.

Field Studies. Field studies were conducted in our experimental field located in Tsukuba City, Japan, and started on May 12, 2015. The daily mean temperature of Tsukuba City during the experiment ranged from 16 to 30 °C (mean of 23 °C). The characteristics of the field soil (FS) are listed in Table 1. Ten pesticides, dinotefuran, imidacloprid, clothianidin, thiacloprid, fosthiazate, metalaxyl, fenobucarb, flutolanil, procymidone, and tolclofos-methyl, were used in the field study (Table 2). One liter of a mixed solution of the 10 pesticides (200 mg/L each), prepared by water dilution of commercial formulations (i.e., emulsifiable concentrates, water-soluble powders, and water-dispersible powders), was evenly applied to triplicate plots (1 m \times 1 m) using a watering can. Subsequently, the soil surface (approximately 0–20 cm depth) was tilled with a walking-type tilling apparatus. The initial concentration of pesticides in the 0–20 cm soil depth after tilling was calculated using the actual bulk density (0.45 g/cm³) and was 2.2 $\mu\text{g}/\text{g}$ of DW for each pesticide. Four cores were taken from each plot 0 (immediately after tilling), 2, 7, 14, 21, 28, 35, 42, 49, 56,

63, 70, 77, and 84 days after application of the pesticides using cylindrical cans (8 cm inner diameter, 10 cm depth). The cores were combined for each plot and were mixed well. An approximately 15 g sample of the soil was dried at 105 °C to measure the moisture content, and an aliquot equivalent to 5 g of DW was analyzed using a sequential extraction method in the same way that was used in the laboratory experiment; i.e., the samples were first extracted three times with 25 mL of distilled water for 24 h at 25 ± 2 °C and subsequently with 30 mL of acetone for 20 min at 25 ± 2 °C.

RESULTS AND DISCUSSION

Dissipation Behavior of Water-Extractable and Total Extractable Pesticides in Laboratory Studies. The

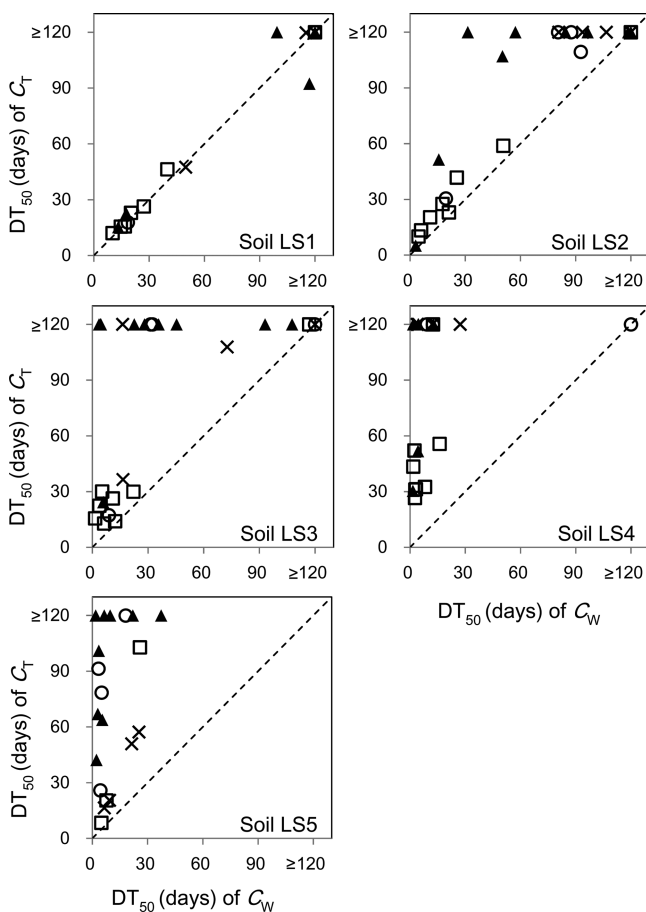


Figure 1. Comparison of DT_{50} values between water extracts (C_W) and total extracts (C_T) from soil: (O) neonicotinoids, (□) organophosphates, (▲) fungicides, and (×) others. The dashed line shows the 1/1 line.

applicability of a sequential extraction method was verified on the basis of the mass balance (MB, %), which was calculated by dividing the C_T value by the initial concentration of pesticides in soil, of the sample after incubation for 0 days (Supporting Information section SI-2). The MB differed depending on the type of pesticide and type of soil. From the results of recovery tests, i.e., the mean recovery of pesticide in water and soil samples was $\geq 73.2\%$ (see Materials and Methods, Pesticide Analysis), when the MB was $< 70\%$, the method was judged to be inapplicable because of biodegradation or hydrolysis during the 24 h water extraction. The MB of several pesticides, especially in LS5, was $< 70\%$, and these samples were excluded from the succeeding data analysis.

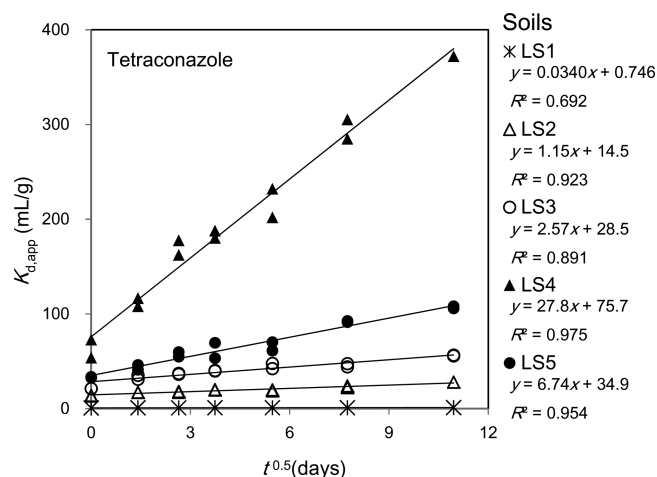


Figure 2. Time-dependent changes in the apparent sorption coefficient ($K_{d,app}$) of tetraconazole.

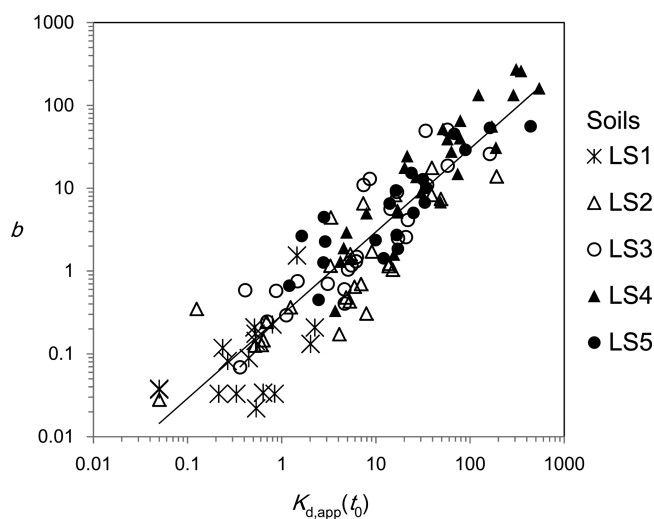


Figure 3. Fitted parameter b for eq 7 plotted as a function of apparent sorption coefficient for the 0 day incubation [$K_{d,app}(t_0)$].

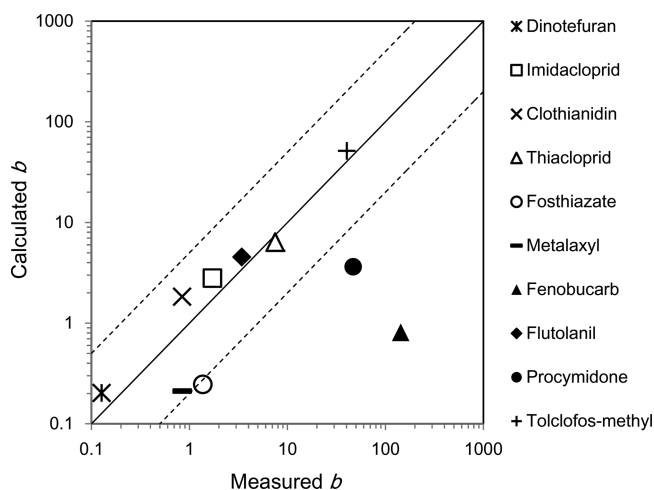


Figure 4. Comparison between measured and calculated b values for eq 7. The solid line shows the 1/1 line, and the dashed lines show the 1/5 and 5/1 lines.

Figure 1 shows a comparison of the DT_{50} values of C_W and C_T . The DT_{50} values were calculated using two kinetic models,

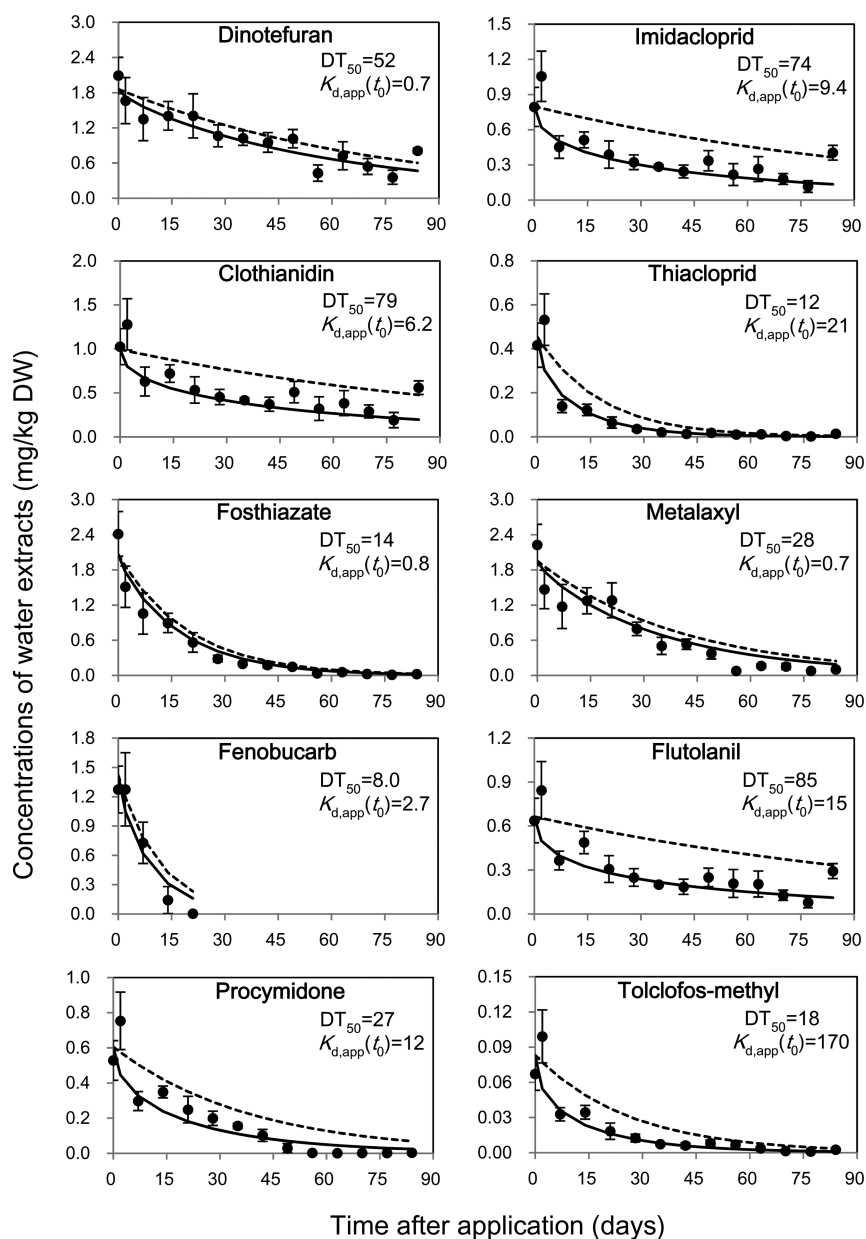


Figure 5. Comparisons between calculated and measured concentrations of water extracts from soil: (●) measured values, (—) values predicted using apparent sorption coefficients calculated by eq 9, and (---) values predicted using the apparent sorption coefficient of the 0 day incubation [$K_{d,app}(t_0)$ (milliliters per gram)]. DT_{50} (days) indicates the values of total extracts from soil calculated by eq 5. Error bars indicate the standard error. The measured values of fenobucarb were less than the LOQ on day 28 and after 28 days.

SFO and DFOP. The goodness of fit to the individual models was verified using the model error calculated by the χ^2 value,²⁴ and the DT_{50} values calculated by the model that had the smaller error level were adopted in Figure 1. The DT_{50} values of C_T were greater than those of C_W for all test soils except soil LS1. The details of the DT_{50} values and error levels for each model are summarized in Supporting Information section SI-2. The error levels of the two models of C_T were approximately equal to each other. In contrast, the error levels of the DFOP model of C_W were smaller than those of the SFO model, especially for soil LS4. Furthermore, previous research²⁶ on the dissipation of pharmaceuticals, which are organic chemicals as well as pesticides, in soil pore-water was better fitted to the biphasic DFOP and first-order multicompartiment (FOMC) models rather than the SFO model. Although our chemicals are not classified as pharmaceuticals, these results suggest that the

dissipation of water-elutable or water-extractable organic chemicals in soils is better described by biphasic models.

For the DT_{50} of C_T , many fungicides showed relatively high values among the tested compounds, and in particular, the values of metalaxyl, boscalid, procymidone, tetraconazole, and diclocymet were >120 days for all soil samples (Supporting Information section SI-2). Japanese registration data also show long DT_{50} values (>100 days) for boscalid and diclocymet under laboratory conditions.²⁷ On the other hand, the DT_{50} values of organophosphorus compounds such as dimethoate, fosthiazate, methidathion, fenitrothion, diazinon, tolclofos-methyl, and fenthion were relatively low. It was reported that the organophosphorus pesticides such as diazinon, dimethoate, and fenitrothion could be easily degraded by microorganisms; in other words, the DT_{50} values of these pesticides were ≤ 41 days.²⁸ Focusing on the differences among test soils, we found

Table 3. Statistical Analysis of the Measured and Predicted Concentrations of Water Extracts from Soil

soil	compound	uniform sorption ^a		time-dependent sorption ^b	
		RMSE ^c	NSE ^d	RMSE ^c	NSE ^d
FS	dinotefuran	58.8	0.78	53.1	0.97
	imidacloprid	80.7	0.05	52.5	0.88
	clothianidin	71.1	0.20	51.0	0.90
	thiacloprid	70.4	0.82	64.4	0.87
	fosthiazate	44.8	0.92	36.0	0.97
	metalaxyl	60.0	0.82	51.3	0.95
	fenobucarb	15.7	0.97	14.5	0.95
	flutolanil	87.9	-0.21	51.2	0.88
	procymidone	82.6	0.71	62.9	0.87
	tolclofos-methyl	74.7	0.73	63.9	0.84

^aPrediction using the apparent sorption coefficient for the 0 day incubation. ^bPrediction using apparent sorption coefficients calculated by eq 9. ^cRoot-mean-square error (%). ^dNash–Sutcliffe model efficiency.

soil L55 indicated relatively low DT₅₀ values of C_T for various pesticides as well as organophosphates. The dissipation of a pesticide is thought to be affected by photolysis, hydrolysis depending on soil pH, and biodegradation.²⁹ In this study, the incubation of soil samples was conducted in a dark place, and the pH of soil L55 was almost the same as the pH of soils LS3 and LS4. Therefore, hydrolysis and photolysis seemed not to be a direct cause of the fast dissipation of pesticides in soil L55, and thus, biodegradation is thought to be the main contributor to dissipation.

Unlike the dissipation behavior of C_T, the DT₅₀ values of C_W for many pesticides tended to decrease in the following order of soils: LS1 ≥ LS2 ≥ LS3 ≥ LS5 ≥ LS4. The DT₅₀ values of C_W in soil LS1 with an extremely low OC content were longer than those of the other soils and exhibited a trend similar to those of C_T. On the other hand, the dissipation of C_W of two andisols (LS4 and LS5) having high OC content was faster than that of other soils. The OC content tends to be positively correlated with microbial activity in soils, and a positive correlation between the degradation rate of weakly sorbed compounds with high bioavailability and OC contents of soils has often been reported.^{30,31} Because C_W is the readily bioavailable fraction,^{9,13} the DT₅₀ of C_W seemed to vary depending on microbial activity, which is influenced by the OC content of the soils. However, if we focus on the results of soils LS4 and LS5, the DT₅₀ values of soil LS4 for many pesticides, especially for hardly degradable fungicides, were lower than those of soil LS5, which had the highest OC content (Supporting Information section SI-2). Furthermore, it is known that the dominant sorbent in soils of nonionic pesticides is organic matter consisting of OC.¹⁶ Therefore, there is a possibility that the sorption of pesticides to OC affects the dissipation of C_W; i.e., the DT₅₀ values decrease with an increase in the K_d values. According to our previous report,²⁰ the K_d values obtained in the standard batch sorption tests⁵ were higher for soil LS4 than for soil LS5 because of the difference in the organic carbon quality; i.e., soil LS4 had an aromatic carbon content higher than that of soil LS5 and an O-alkyl carbon content lower than that of soil LS5. Several reports show that the OC-normalized sorption coefficients (K_{oc}) of pesticides were positively correlated with aromatic carbon content and negatively correlated with O-alkyl carbon content.^{20,32–34}

The dissipation of C_W showed a behavior different from that of C_T. The reason for this is that the dissipation of C_W, which is the readily bioavailable fraction, is more affected by biodegradation than that of C_T. Furthermore, the dissipation of C_W is also affected by the soil sorption, making the investigation of sorption properties, especially time-dependent changes in K_d, necessary for better understanding the contribution of soil sorption to the dissipation of C_W.

Time-Dependent Sorption in Laboratory Studies. As mentioned in previous reports,^{6–15} the K_{d,app} values of many pesticides increased with an increase in incubation time. It is suggested that the time-dependent changes in soil sorption are attributed to the slow diffusion of pesticides into organic matter and the nanopore structures in soil particles.³ The pesticides are considered to move from the surface site of the soil particles to the interior sites, i.e., less accessible sites, with aging time. According to previous reports,^{10,12,14} the changes in K_{d,app} with time could be represented as

$$K_{d,app} = a + bt^{0.5} \quad (7)$$

where *a* and *b* are empirical parameters and *t* is the time of incubation. Although this empirical equation has no theoretical basis, it is suggested that the amounts of sorbed chemicals, which are controlled by diffusion, are proportional to the square root of time.^{35,36} Figure 2 shows an example of tetraconazole to illustrate the time-dependent changes in sorption. The details of the linear regression analysis for all pesticides are summarized in Supporting Information section SI-3. The soil samples, except for soil LS1, exhibited significant positive correlation (*P* < 0.05) between the K_{d,app} values and the square root of time for many pesticides. In the case of soil LS1, which has the lowest OC content, the time-dependent increase in K_{d,app} was not observed for many pesticides and the coefficient of determination values (*R*²) were extremely low.

Parameters *a* and *b* play an important role in the prediction of time-dependent changes in the K_{d,app} values. When a good fit to eq 7 was achieved, the *a* and *b* values were relatively high, with the condition that the OC content of soils and the log *P*_{ow} of pesticides were both high and the log *S*_w of the pesticides was low (Supporting Information section SI-3), i.e., the condition of an increasing level of soil sorption of nonionic pesticides,¹⁶ and the *a* values, which represent K_{d,app} at time zero, were approximated as the measured K_{d,app} values of the 0 day incubation sample [K_{d,app}(*t*₀)] (Supporting Information section SI-3). Moreover, the *b* values were proportional to the K_{d,app}(*t*₀) values, as shown in Figure 3. The linear regression equation describing the relationship between *b* and K_{d,app}(*t*₀) is

$$\log b = -0.532 + 1.005 \times \log K_{d,app}(t_0) \quad (8)$$

with *R*² = 0.838, *P* < 0.001, and *n* = 116. Thus, eq 8 suggests that parameter *b* can be estimated using the K_{d,app}(*t*₀) values that roughly indicate the degree of sorption to the surface sites of soil particles. Li et al.³⁷ investigated the soil sorption of atrazine using batch experiments combined with an online microfiltration (MF)–high-performance liquid chromatography technique; they showed that the intraparticle diffusion rate was proportional to labile surface sorption, i.e., labile surface coverage. In the study presented here, it is hard to clearly distinguish labile surface sorption from nonlabile sorption caused by intraparticle diffusion because K_{d,app}(*t*₀) is likely to include a small degree of nonlabile sorption occurring rapidly during the water extraction time of 24 h. However, the positive

correlation between the $K_{d,app}(t_0)$ values and the b values of eq 7, i.e., the increased rate of $K_{d,app}$, implies that a slow diffusion process contributes to the time-dependent increase in $K_{d,app}$. However, Supporting Information section SI-3 also shows that the easily degradable pesticides such as methidathion, fenitrothion, kresoxim-methyl, and fenthion, which have low DT_{50} values of C_T (Supporting Information section SI-2), exhibit relatively high b values for $K_{d,app}(t_0)$. Cox et al.⁶ and Koskinen et al.⁸ reported that the time-dependent increase in K_d values for imidacloprid and its metabolites was due to degradation in solution and on labile sites when the degradation rate was higher than the rate of desorption from soil. Thus, the time-dependent increase in $K_{d,app}$ in this study was thought to be affected not only by diffusion into nonlabile sites but also by fast dissipation in solution and on labile sites.

Although two reasons may contribute to the time-dependent increase in $K_{d,app}$, the empirical relationships between $K_{d,app}(t_0)$ and the parameters of eq 7 (a and b) allow us to rewrite eq 7 by using $K_{d,app}(t_0)$ as

$$K_{d,app} = K_{d,app}(t_0) + 0.294K_{d,app}(t_0)^{1.005}t^{0.5} \quad (9)$$

Thus, it appears to be possible to estimate the time-dependent changes in the $K_{d,app}$ values based on the $K_{d,app}(t_0)$ values.

The soil sorption, given as $K_{d,app}$ values, of pesticides increased with time. The rate of the increase in $K_{d,app}$ with time was high when $K_{d,app}(t_0)$, which represented the initial sorption strength, was high. As mentioned in Dissipation Behavior of Water-Extractable and Total Extractable Pesticides in Laboratory Studies, the DT_{50} values of C_W decreased with increasing K_d values without previous incubation. Therefore, it is suggested that the dissipation of C_W is influenced by the time-dependent increase in soil sorption. Taking this into account is important for predicting the dissipation of C_W .

Prediction of Water-Extractable Pesticides in a Field.

The field study was conducted to validate the estimation method of the time-dependent $K_{d,app}$ based on $K_{d,app}(t_0)$ suggested by the laboratory study. The time-dependent changes in the $K_{d,app}$ values in the field study were fitted to eq 7. Supporting Information section SI-4 shows the details of the linear regression analysis between the $K_{d,app}$ values and the square root of time. Figure 4 shows that measured b values for all pesticides, except for fenobucarb and procymidone, are in good agreement with predicted b values using eq 8. The measured b values of fenobucarb and procymidone exceeded the predicted values by ≥ 10 -fold. The $K_{d,app}$ values of fenobucarb and procymidone were extremely high on days 14 and 49 and after 14 and 49 days, respectively, and the fit to eq 7 for these two pesticides was poor ($R^2 < 0.3$), as shown in Supporting Information section SI-4. This is likely because the C_{aq} values, i.e., the concentrations of pesticides in the aqueous phase, for two pesticides decreased up to a level near the LOQ with time.

As discussed in Dissipation Behavior of Water-Extractable and Total Extractable Pesticides in Laboratory Studies, the dissipation behaviors of C_W and C_T differed from each other; i.e., the dissipation of C_T could be described by the SFO model, whereas the dissipation of C_W was more rapid than that of C_T and was better fitted to the biphasic model. As the reason for this, the time-dependent increase in soil sorption was thought to affect the dissipation of C_W . Therefore, the prediction of dissipation of C_W was performed by compensating for the

dissipation of C_T using the time-dependent $K_{d,app}$. The predicted C_W was determined using the following equation:

$$C_W = C_T \frac{r}{r + K_{d,app}} \quad (10)$$

where C_T was calculated using the SFO model (eq 3) and r is the ratio of solution to soil (milliliters per gram) of water extraction (the mean value of the field study was 5.6). The $K_{d,app}$ calculated by eq 9 and $K_{d,app}(t_0)$ were used in eq 10 with and without consideration of time-dependent sorption, respectively. The goodness of fit to each estimation method was assessed using the root-mean-square error (RMSE) and the Nash–Sutcliffe model efficiency (NSE) calculated by the following equation:^{38,39}

$$RMSE = \frac{100}{\bar{O}} \sqrt{\frac{1}{n} \sum_{i=1}^n (P_i - O_i)^2} \quad (11)$$

$$NSE = \left[\sum_{i=1}^n (O_i - \bar{O})^2 - \sum_{i=1}^n (O_i - P_i)^2 \right] / \sum_{i=1}^n (O_i - \bar{O})^2 \quad (12)$$

where P_i and O_i are the predicted and observed values, respectively, \bar{O} is the average of the observed values, and n is the number of observations.

Figure 5 shows the comparison between the measured C_W and the predicted C_W values with and without consideration of the increase in $K_{d,app}$ with time. In the case of pesticides having low $K_{d,app}(t_0)$ values (< 1 mL/g), such as dinotefuran, metalaxyl, and fosthiazate, the predicted values with and without consideration of the time-dependent $K_{d,app}$ almost coincided with each other. On the other hand, when the $K_{d,app}(t_0)$ values of pesticides were > 6 mL/g, the C_W values predicted using the $K_{d,app}(t_0)$ values overestimated the measured values. The differences between the values predicted using the $K_{d,app}(t_0)$ values and the measured values, especially for clothianidin, imidacloprid, and flutranil, were larger than those for other pesticides. In contrast, the C_W values predicted using $K_{d,app}$ estimated by eq 9 showed good agreement with the measured C_W values. Table 3 shows RMSE and NSE values for each pesticide. The RMSE values calculated using the C_W values predicted by time-dependent $K_{d,app}$ were lower than those predicted by the $K_{d,app}(t_0)$ values. Furthermore, the NSE values were closer to 1 when the time-dependent increase in $K_{d,app}$ was considered. In particular, the NSE values of clothianidin, imidacloprid, and flutranil were obviously improved with the consideration of time-dependent sorption. These three pesticides had DT_{50} values of C_T higher than those of other pesticides. When the dissipation of C_T was slow, the prediction of C_W using $K_{d,app}(t_0)$ was inadequate and the consideration of time-dependent sorption was required for prediction of C_W . Thus, the estimation method of C_W using the dissipation of C_T and the time-dependent $K_{d,app}$, which was calculated by eq 9, was capable of reproducing the biphasic dissipation of the measured C_W .

Our results demonstrate that dissipation of C_W was faster than that of C_T , and the time-dependent increase in $K_{d,app}$ affected the difference in the dissipation rate between C_W and C_T . Therefore, it is possible that the dissipation of C_W , which can be used to assess phytoavailability, is predicted by correcting the dissipation of C_T by time-dependent $K_{d,app}$. The increased rates of $K_{d,app}$ with time were proportional to

$K_{d,app}(t_0)$ values, and this empirical relationship suggests that $K_{d,app}(t_0)$ plays an important role in the prediction of the time-dependent increase in $K_{d,app}$ and dissipation of C_W . The estimation method, which predicted the dissipation of C_W using the time-dependent $K_{d,app}$ calculated on the basis of $K_{d,app}(t_0)$, was demonstrated in the field study. These results imply that the residual concentrations in leafy vegetables cultivated in pesticide-contaminated soils can be estimated before sowing by using the correlations between the C_W values at harvesting time, which were predicted by the estimation method described above, and the uptake concentrations for the vegetables reported in our previous study.⁴

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jafc.6b01028.

Sections SI-1–SI-4, including Tables S1–S7 (PDF)

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Funding

This research was supported by the Environmental Research and Technology Development Fund (5-1302) of the Ministry of the Environment, Japan.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Shintaro Kanbayashi (Wesada University, Tokyo, Japan) for his help with laboratory studies. The test soils were kindly supplied by Aichi Agricultural Research Center and Tochigi Prefectural Agricultural Experiment Station.

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