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Original Article

Aerobic Aquatic Soil Metabolism of Pesticides in Water- and Sediment-Spiked Systems

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The metabolism of fenitrothion and diethofencarb in aerobic aquatic soil was examined following either water or sediment application. The more hydrophobic fenitrothion rapidly distributed from water to sediment, while a more gradual adsorption of diethofencarb by sediment was observed with insignificant biodegradation. Release of diethofencarb from the spiked sediment was observed but degradation via ester cleavage and reduction of the nitro group with more bound residues resulted in less of a release of fenitrothion into water. The distribution profiles of the pesticides and their metabolites depended on their adsorption and diffusivity in the sediment phase. The TOXSWA program was useful for evaluating the dissipation profiles of the water-applied pesticides.

Keywords: biodegradation, water-sediment system, fenitrothion, diethofencarb, TOXSWA simulation.

INTRODUCTION

Pesticides applied in the field are considered to eventually enter aquatic environments such as rivers, ponds and marshes via spray-drift, run-off and erosion events dependent on the type of formulation, application method and meteorological conditions. The aquatic environment mainly consists of water bodies containing, suspended matter, underlying sediment and various kinds of biota and hence, these components complicatedly affect the behavior of a pesticide.[1] Among controlling factors, either partition to suspended matters and sediment or transformation processes are considered most important in relation to the physicochemical properties of pesticides. In order to investigate the environmental profiles of pesticides in such an aquatic environment, lab-scale water-sediment studies with different experimental conditions were proposed using various test guidelines.[2]

We have recently examined some experimental conditions controlling the behavior of a pesticide in water-sediment systems where the water phase is spiked.[3,4] Through these studies, the partition and transformation processes were found to be rather insensitive to the water-sediment type but chemical structures and the physicochemical properties and aerobicity of the system were found to greatly affect the metabolic profiles. Among physicochemical properties, hydrophobicity and the adsorption coefficient for sediment are the most important.[5,6] Incidentally, the route of entry into an aquatic environment is considered to influence the behavior of a pesticide. Atrazine applied to the water phase of an aerobic water-sediment system was rapidly dissipated via adsorption by sediment together with degradation to its hydroxyl and dealkylated derivatives,[7] while the rapid release of atrazine applied to sediment into overlying water was followed by a slower release due to its biodegradation in the sediment phase.[8] Therefore, the present study was conducted to examine the impact of the application method, that is, the water- and sediment-spike, as a different path of entry into the system each corresponding to spray drift and run-off events, respectively. Two pesticides, fenitrothion (**I**) [*O*,*O*-dimethyl *O*-(3-methyl-4-nitrophenyl) phosphorothioate] and diethofencarb (**II**) [isopropyl 3,4-diethoxycarbanilate], were used as model compounds having different physicochemical properties and metabolic profiles.

MATERIALS AND METHODS

1. *Chemicals*

The chemical structures of **I** and **II** together with those of their relevant metabolites are listed in Table 1. **I** and **II** uniformly labeled with ^{14}C at the phenyl rings were synthesized in our laboratory from the corresponding ^{14}C-labeled phenol and aniline according to reported methods.[9,10] **I** and **II** were

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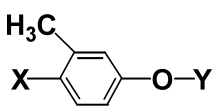
Table 1. Molecular formulae of pesticides and their possible degradation products

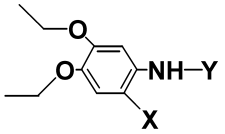
Compound[a)]	X	Y	Rt[b)]
I	NO_2	$P(=S)(OCH_3)_2$	46.6
Ia	NH_2	$P(=S)(OCH_3)_2$	23.0
Ib	$NHCOCH_3$	$P(=S)(OCH_3)_2$	27.3
Ic	NO_2	H	25.2
Id	NH_2	$P(=S)(OH)(OCH_3)$	6.5
II	H	$COOC_3H_7$	30.0
IIa	NO_2	$COOC_3H_7$	37.5
IIb	H	H	12.5

a) Basic chemical structures are shown below.

b) Typical HPLC retention time (in min).



I



II

Table 2. Characteristics of sediment and associated water

Location	Swiss Lake	Japanese Pond
Sediment		
Soil texture (%)		
Sand	45.5	63.7
Silt	51.1	17.1
Clay	3.4	19.2
Soil classification	Silty loam	Sandy clay loam
Organic carbon (%)	1.5	1.3
Bulk density ($kg\,m^{-3}$)	2160	1530
Cation exchange capacity		
(meq per 100 g dry sediment)	7.5	8.1
pH (H_2O)	7.2	5.3
Associated water		
DOC ($mg\,l^{-1}$)	18.0	n.a.
Suspended matter ($g\,m^{-3}$)	48	50
pH	7.5	6.4

n.a.: not analyzed.

purified by thin-layer chromatography (Silica gel $60F_{254}$ thin-layer plates; 20×20 cm, 0.25-mm layer thickness, E. Merck) developed using toluene/ethyl acetate (4/1, v/v; R_f=0.57) for **I** and toluene/acetone (3/1, v/v; R_f=0.67) for **II**. The specific activity and radiochemical purity of **I** and **II** were $6.7\,MBq\,mg^{-1}$ and 97.9%, and $8.8\,MBq\,mg^{-1}$ and 98.5%, respectively. The non-labeled pesticides and their metabolites were also synthesized in our laboratory according to reported methods.[11–13)] The chemical purity of each standard was determined to be >95% by high-performance liquid chromatography. **I**c was purchased from Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan) and used without further purification.

2. Radioassay

The radioactivity in the water layer, extracts of water and sediment and trapping media was individually measured by liquid scintillation counting (LSC) with a Packard model 2000CA liquid scintillation analyzer. The unextractable sediment residue was powdered after drying in a vacuum desiccator and a portion was subjected to combustion analysis using a Packard model 307 sample oxidizer. Details of this radioanalysis have been previously reported.[3)] The radioactivity trapped in the polyurethane foam plug was soaked in 5 ml of methanol and a 1-ml aliquot was quantified by LSC in duplicate.

3. High-Performance Liquid Chromatography

The extracts from water and sediment were individually analyzed by reversed phase high-performance liquid chromatography (HPLC) for analytical purposes. A Hitach L-6200 liquid chromatograph equipped with a Sumipax ODS A-212 column (5 μm, 6-mm i.d.×15 cm, Sumika Analysis Service, Ltd., Osaka) was operated at a flow rate of $1\,ml\,min^{-1}$. The composition of the mobile phase was changed stepwise as follows: 0 min, %A (acetonitrile)-%B (0.01% trifluoroacetic acid), 10:90; 0–10 min, linear, 35:65 at 10 min; 10–30 min, linear, 50:50 at 30 min; 30–55 min, linear, 90:10 at 55 min for **I**; 0 min, %A (acetonitrile)-%B (0.01% trifluoroacetic acid), 10:90; 0–30 min, linear, 90:10 at 30 min; 30–45 min, isocratic for **II**. The column effluent was monitored with both a Hitachi model L-4000 UV detector at 254 nm and a Packard Flow-one/Beta A-100 radio-detector equipped with a 500-μl liquid cell using Ultima-Flo AP® (Packard) as a scintillator. Each ^{14}C peak was identified in HPLC co-chromatography by comparing its retention time with those of non-radiolabeled authentic standards detected by the UV detector. The typical retention times of **I**, **II** and their potential metabolites are listed in Table 1.

4. Metabolism Studies

Natural sediments and associated surface water collected from a Japanese pond (Tondabayashi City, Osaka) and a Swiss lake (Fussacher Bucht) were used for the water-sediment study of **I** and **II**, respectively. The sediment and water were passed through 2-mm and 250-μm sieves prior to use, respectively, to remove stones and plant debris. Their physical and chemical properties are listed in Table 2. A sample of sediment equivalent to 50 g (Swiss lake) or 30 g (Japanese pond) on a dry-weight basis was taken into a two-necked cylindrical glass vessel (5-cm diameter) to a depth of 2.5 cm.

The associated water was gently added to each vessel to a depth of 6 cm above the sediment in accordance with the method prescribed in the BBA guideline.[7] The water-sediment system was pre-incubated in darkness at 20±1°C for 15 days, prior to the application of each pesticide.

The application rates of **I** and **II** to each water-sediment system were adjusted to 39 and 19.6 μg/vessel by considering their field application rates (1 kg and 0.5 kg a.i/ha), respectively, assuming a uniform distribution in the water phase to a depth of 30 cm.[14] The application rates did not exceed the water solubility of the pesticides (21 ppm, **I**; 27 ppm, **II** at 20°C).[15] The profiles of ^{14}C distribution and metabolites were examined for each pesticide applied to water or sediment. In the water-spike application, the acetonitrile solution of each pesticide (95–100 μl) was dropwise fortified to the water surface in each vessel using a microsyringe. When applied to the sediment, after the associated water was siphoned from vessels, the acetonitrile solution of pesticide was applied to the sediment, well mixed with a spatula and then, the pre-incubated water was gently returned without disturbing the sediment. Each vessel containing sediment and water was placed in an incubator and kept at 20±1°C in darkness. CO_2-free air was passed over the water surface in each vessel in sequence to one gas washing bottle containing 300 ml of ethylene glycol, and another containing 350 ml of 0.5 M NaOH solution and a polyurethane foam plug to trap the volatile ^{14}C.

At appropriate intervals, the surface water, sediment and trapping media were sampled in duplicate and analyzed immediately as previously described[3] except for the extraction of sediment. The sediment was separated into an upper (0.5–0.8 cm) and lower (1.7–2.0 cm) layer with a spatula. The upper layer of both sediments was light brown, while the lower one showed a different color, dark brown (Japanese pond) and dark gray (Swiss lake), which was likely to correspond to the difference of aerobicity.[16] A portion of each sediment was placed on filter paper which was attached to a stainless steel sieve in a centrifugal bottle and subjected to centrifugation at 7000 rpm and 4°C for 20 min to separate the pore water. The sediment was then extracted with ethyl acetate and 0.2 M HCl (2/1, v/v) for **I** or acetonitrile and 0.1 M HCl (4/1, v/v) for **II** as described previously,[3] and the concentrated extracts were analyzed by HPLC. The associated water and the combined pore water from the two layers of sediment were separately extracted by partitioning three times with ethyl acetate, and subjected to HPLC analysis.

5. *Kinetic Analysis*

The half-life (DT_{50}) of each pesticide was estimated assuming first-order kinetics using Microsoft Excel 2000 (Microsoft). In order to examine the dissipation profiles of the pesticide and its metabolites in the water-sediment system in more detail, a kinetic analysis based on the assumed compartments was conducted, using the Model-Maker program (version 4, SB ModelKinetics), as previously reported.[3,4] Since the processes of diffusion among sediment, associated water and sediment pore water are not taken into account in the compartment model, a more sophisticated analysis was also conducted, using the TOXSWA program (version 1.2)[17] according to the recommended method adjusted to analyze a small-scale water-sediment system.[2] The experimental conditions in this study together with the data listed in Table 2 were used for simulation. The TOXSWA program was operated assuming a constant concentration of each pesticide in the horizontal direction in both water and sediment layers whose depths were 6 and 2.5 cm, respectively. The sediment layer was conveniently separated into several compartments each with a thickness of 3–17 mm to simulate the diffusion of each pesticide in it. The soil adsorption coefficient (Koc) of **I** (440)[15] was used as a surrogate of the sediment Koc. In the case of **II**, the sediment Koc value was determined by the batch method[18] to be 70.8. Other parameters necessary for simulation were used as defined in the program. Under these conditions, the half-lives of each pesticide due to transformation ($T_{1/2}$) in water and sediment phases were stepwise changed by 1 to 210 days from those estimated by the first-order kinetics and manually optimized as the variance between the observed and calculated values became minimum.

RESULTS AND DISCUSSION

1. *Aerobic Aquatic Soil Metabolism of* ***I***

The distribution of radioactivity in the Japanese pond water-sediment system is summarized in Table 3. Throughout the experiment, the total radioactivity recovered from the system ranged from 88.3% to 101.8% of the applied ^{14}C. Upon application to the water phase, the radioactivity gradually decreased mainly due to adsorption by the sediment (62.6% after 31 days). Release of ^{14}C from the treated sediment into the surface water was less than 16.9% of the applied ^{14}C and 85.1% remained in the sediment after 31 days. Irrespective of the application method, most of the ^{14}C in the sediment was found to be unextractable and volatile ^{14}C mainly consisted of carbon dioxide, amounting to 5.6% after 31 days in both cases. The radioactivity in the pore water amounted to less than 4%. Furthermore, the volume of collected pore water was approximately 10 ml on average and the relative volumetric ratio to the overlying water was about 1/12. Therefore, the ^{14}C concentration in the pore water could be estimated to be 0.4–0.8 and 2–6-fold that in the overlying water in the water- and sediment-spike after 7 days, respectively.

When applied to water, **I** in the aqueous phase decreased with a DT_{50} value of 4.3 days ($r^2=0.835$) to less than 1% after 31 days. The amount of **I** in the sediment concomitantly increased to a maximum value of 23.7% at day 7 and then decreased to 0.6%, most of which was present in the upper layer (20.8% at day 7) (Fig. 1). As with incubation, a small portion of **I** was also present in the lower sediment layer (1–3%), which can be accounted for by the diffusion process in sediment. The similar downward distribution has been reported

Table 3. Distribution of radioactivity in water-sediment systems

Pesticide	Spike method[b)]	Compartment	Percentage of applied ^{14}C					
			(Days after application)					
			0	1	7 (8)[a)]	14	21 (22)	31
I	W	Associated water	97.7	92.3	52.6	74.8	48.0	19.2
		Upper sediment (B[c)])	1.3 (0.1)	8.4 (0.3)	35.6 (9.3)	14.1 (8.9)	24.6 (18.9)	45.7 (41.5)
		Lower sediment (B)			4.6 (1.1)	3.9 (2.2)	18.6 (12.8)	16.9 (13.5)
		Pore water	0.1	0.2	2.4	2.6	3.2	0.7
		Volatiles	na	<0.1	0.3	1.0	2.0	5.6
I	S	Associated water	3.3	3.4	7.4	16.1	16.9	2.1
		Upper sediment (B)	92.7 (5.0)	8.1 (1.9)	22.0 (16.3)	17.4 (14.2)	19.8 (16.6)	36.4 (33.2)
		Lower sediment (B)		84.3 (30.2)	59.4 (47.9)	55.5 (47.3)	47.5 (39.5)	48.7 (43.0)
		Pore water	1.2	2.0	4.0	4.2	3.7	1.2
		Volatiles	na	<0.1	0.7	1.4	2.6	5.6
II	W	Associated water	97.9	97.2	81.0	75.8	77.1	43.4
		Upper sediment (B)	0.5 (<0.1)	0.8 (0.1)	11.7 (3.5)	10.3 (2.6)	8.2 (2.3)	24.2 (13.3)
		Lower sediment (B)		0.9 (0.2)	4.3 (1.0)	9.6 (2.6)	9.6 (2.7)	20.5 (7.4)
		Pore water	0.1	0.3	1.4	1.9	1.8	1.9
		Volatiles	na	0.2	0.7	1.1	1.6	2.3
II	S	Associated water	12.8	26.6	33.1	30.5	35.1	33.6
		Upper sediment (B)	66.4 (4.6)	60.1 (11.8)	44.7 (13.6)	46.1 (14.5)	42.7 (16.6)	41.1 (17.6)
		Lower sediment (B)		10.1 (1.2)	11.9 (2.6)	17.4 (7.7)	13.9 (4.4)	15.1 (5.7)
		Pore water	11.8	6.1	4.0	4.5	2.7	2.6
		Volatiles	na	<0.1	0.1	0.3	0.5	0.8

a) Sampling days in parentheses for **II**. b) W and S mean the water- and sediment spike, respectively. c) % of bound ^{14}C.

for fenthion which diffused to a depth of approximately 2.5 cm in a sterile water-sediment system.[19)] The corresponding DT_{50} value of the total system was estimated to be 4.9 days ($r^2=0.866$). Since **I** is known to exhibit a moderate abiotic hydrolysis at pH 5–7 with half-lives of 40–80 days,[20)] a more rapid dissipation in these water-sediment systems would imply the involvement of biotic processes. HPLC analysis showed that the major metabolites in the water phase were **I**a, **I**c and **I**d, each amounting to 7.4% (day 21), and 8.8% (day 7) and 7.1% (day 21), respectively. No trace amount of the oxon derivative of **I** could be detected, irrespective of the application method. The former two metabolites were also detected in the upper layer of sediment, each amounting to 3.9% (day-21) and 4.5% (day-7), respectively. **I**b was detected as a minor metabolite in both phases, amounting to less than 4% in total. **I** primarily underwent either cleavage of the P-O aryl linkage to form **I**c or reduction of the nitro group to **I**a, as previously reported,[2)] and the latter reaction was a somewhat slower process. The successive acetylation of the amino group or *O*-demetylation of **I**a gave **I**b and **I**d in the later period of incubation. As in the water, **I**c was also distributed in the upper layer of sediment and showed a maximal value of 4.1% after 7 days. Similar trends were observed for **I**a and **I**b with small amounts (0.3–1.3%) being detected in the lower sediment layer, indicating their diffusion in the sediment via pore water. No amount of **I**d was detected in the sediment, which was likely to be due to its higher hydrophility.

In the case of the sediment application, a similar DT_{50} value (6.3 days, $r^2=0.845$) was obtained for **I** in the total system. As shown in Fig. 2, less **I** was distributed in the upper than lower layer and **I** in the aqueous phase gradually decreased from 4.3% at day 0 to less than 1% at 14 days. The same metabolites in the water-spike case were detected in both phases but with a different distribution. **I**c was also formed in the early stage of incubation (at day 0–3) but showed a more rapid dissipation in the sediment with a gradual increase in the water phase. Microbial degradation of **I**c together with its distribution in the water phase *via* diffusion through pore water most likely accounted for these profiles. The situation was similar for the other metabolites and a higher hydrophilicity resulted in a more extensive distribution in the water phase.

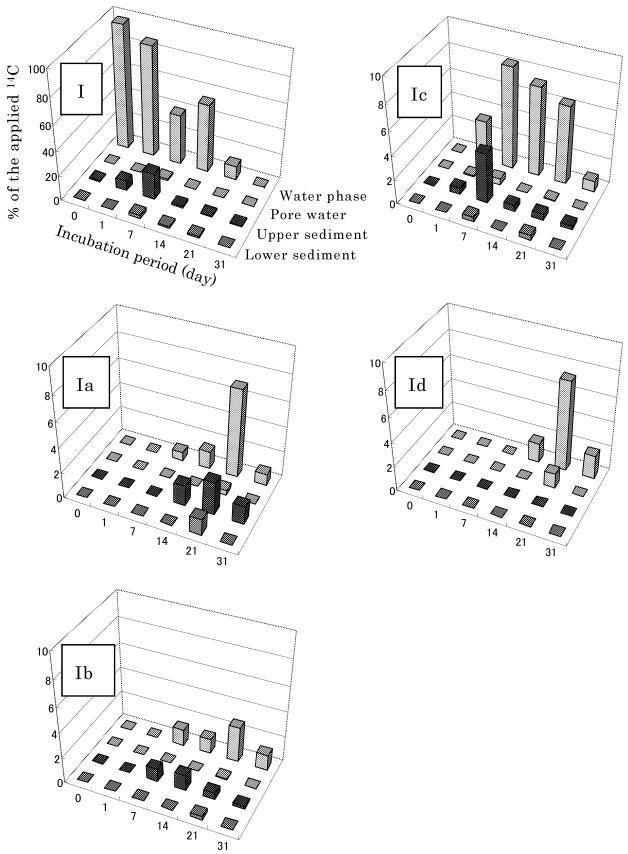


Fig. 1. Distribution of **I** and its metabolites in the Japanese pond water-spiked system.

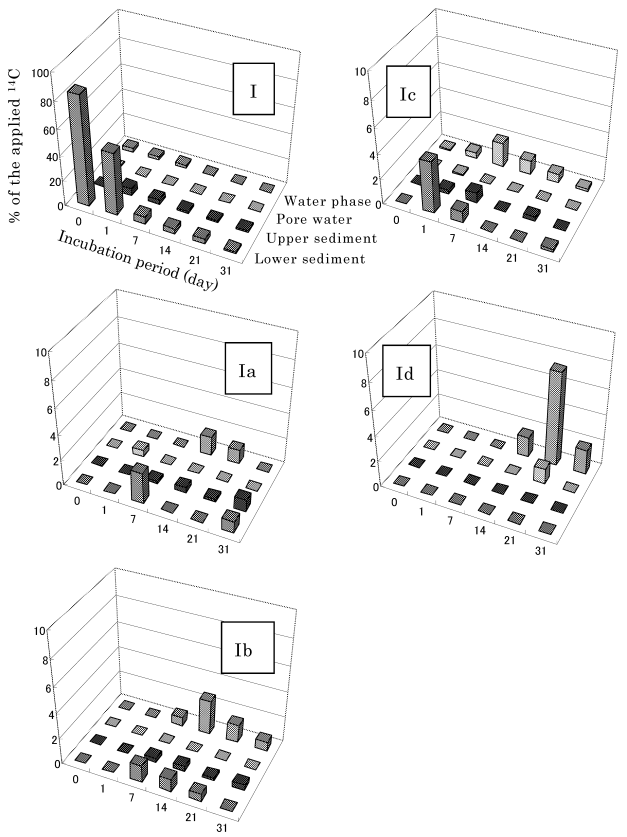


Fig. 2. Distribution of **I** and its metabolites in the Japanese pond sediment-spiked system.

*2. Aerobic Aquatic Soil Metabolism of **II***

The distribution of ^{14}C in the Swiss Lake water-sediment system is summarized in Table 3. The total recovery of ^{14}C ranged from 91.0% to 103.1% of the applied dose. As compared with **I**, a slower adsorption of **II** with less of a distribution in the sediment (44.7% after 31 days) was observed when **II** was applied to the water phase. In the case of the sediment-spike, a great release of ^{14}C into the water phase, amounting to 35.1% of the applied ^{14}C at maximum, was observed. The volatile ^{14}C amounted to less than 3% of the applied ^{14}C. Approximately half of ^{14}C in the sediment originated from the bound residues. As compared with **I**, more **II** was detected in the pore water especially in the early stage of incubation (6–12% for up to 3 days) but the amount gradually decreased thereafter, which might be due to the smaller Koc value of **II** (270) than **I** (440).[15] A lower ^{14}C concentration in the pore water than the overlying water was detected after 7 days (0.2–0.5 and 0.5–1.7 for water- and sediment-spike), possibly due to the lower Koc value of **II**.

HPLC analysis of the water and sediment extracts showed insignificant degradation of **II** in each phase where each unknown amounted to less than 2–3%. The unique soil metabolite (**II**a) formed via nitration at the 6-position of the 3,4-diethoxyphenyl moiety of **II**[21] could not be detected in these water-sediment systems. Furthermore, the corresponding aniline (**II**b) formed via cleavage of the carbamate linkage could not be detected, either. Since alkyl *N*-arylcarbamate including **II** is known to be generally resistant to hydrolysis under environmental conditions,[20] the absence of **II**b showed the insignificance of the biotic cleavage of the carbamate linkage. In contrast to **I**, **II** dissipated more slowly with DT_{50} values of 24.2 days (r^2=0.945, water phase) and 45.3 days (r^2=0.915, total system) mainly due to adsorption by the sediment, when **II** was applied to the water. A longer DT_{50} value (68.9 days, r^2=0.953) was calculated for the total system in the sediment-spike case. The different profiles in the water-sediment system between **I** and **II** were accounted for by the extent of metabolic degradation and hydrophobicity of the pesticides. The Koc values in the soil were measured as 440 (**I**) and 270 (**II**) and hence, the higher adsorption with faster metabolic degradation of **I** resulted in the shorter lifetime in the water-sediment system.

3. Kinetic Analysis

On the basis of the distribution profiles of **I** in the water-sediment system, the four compartments of water, sediment, bound residues and volatiles were considered for kinetic analysis, as shown in Fig. 3. The upper and lower layers was combined as one sediment phase. Others and volatiles refer

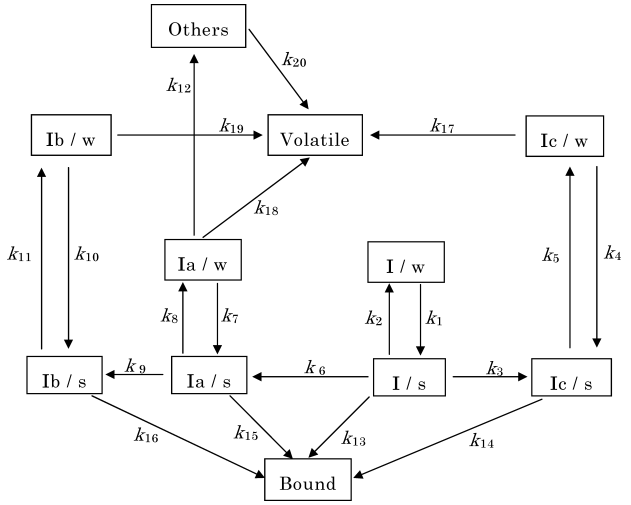


Fig. 3. Compartment model used for kinetic analysis of degradation of **I**. "w" and "s" mean the water and sediment phases, respectively.

Table 4. Kinetic analysis of the degradation of **I** and **II** based on compartment models

	I[a)]		**II**[b)]
Rate constant	k_1: 0.351	k_{11}: 0.040	k_1: 0.636
(day^{-1})	k_2: 0.150	k_{12}: 0.094	k_2: 0.461
	k_3: 0.063	k_{13}: 0.410	k_3: 0.020
	k_4: 0.068	k_{14}: 0.022	k_4: 0.002
	k_5: 0.055	k_{15}: 0.002	—
	k_6: 0.133	k_{16}: 0.007	—
	k_7: 6.363	k_{17}: 0.100	—
	k_8: 2.693	k_{18}: 0.100	—
	k_9: 0.080	k_{19}: 0.051	—
	k_{10}: 0.007	k_{20}: 0.001	—
$r^{2c)}$	0.947		0.859

a) Sediment-spike, Japanese pond water-sediment system. Compartment in Fig. 3 was used. b) Sediment-spike, Swiss lake water-sediment system. Compartment in Fig. 4 was used. c) Coefficient of correlation.

to the total amounts of **I**d and unknown degradates, and carbon dioxide, respectively. There were so many rate constants (twenty including k_1–k_{11}) for the analysis that the optimization from any initial rate constant failed to well describe the profiles of **I**–**I**d in the water-spike case. The analysis of the sediment-spike case gave a rather good correlation (r^2=0.947) when the optimized rate constants in Table 4 were used. Although the distribution profiles of **I** between water and sediment and formation of bound residues and carbon dioxide

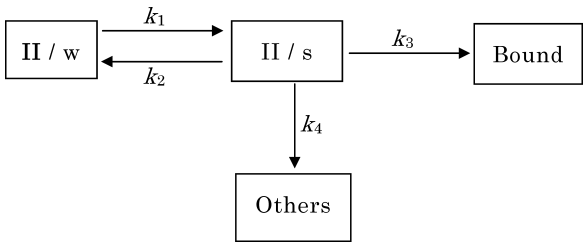


Fig. 4. Compartment model used for kinetic analysis of degradation of **II**. "w" and "s" mean the water and sediment phases, respectively.

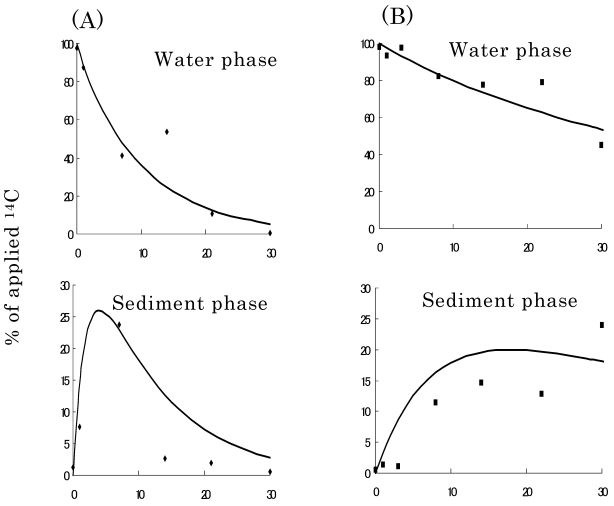


Fig. 5. Decline of **I** and **II** in water and sediment phases simulated by TOXWA. (A) **I** in the water-spiked Japanese pond water-sediment system. (B) **II** in the water-spiked Swiss lake water-sediment system.

could be well estimated, the curves of formation and decline for **I**a–**I**c in each phase were over-estimated by a factor of 2–3. This poor result was likely to stem from data fluctuation in the small-scale systems and because the diffusion at the water-sediment interface was not considered. In the case of **II**, the approach with the compartment model (Fig. 4) failed to describe the distribution of **II** when applied to the water. In the case of the sediment-spike, the k_1–k_4 values listed in Table 4 well resembled the experimental results. The total rate of bound formation for **I** (0.44 day^{-1}, $k_{13}+k_{14}+k_{15}+k_{16}$) was much larger than the k_3 value (0.02 day^{-1}) for **II**, which well explained the less bound formation for **II**.

Alternatively, the distribution of **I** and **II** in the water-sediment systems when the pesticide was applied to the water was analyzed using the TOXSWA program. The curves of decline and formation in each phase could be well simulated as shown in Fig. 5. The sediment layer was divided into 3 segments with a thickness of 3, 5 and 17 mm from the top for **I** and into two segments (10 and 15 mm) for **II**, which resulted in the best simulation. The optimized $T_{1/2}$ values for **I** are 42 days and 2 days in the water and sediment phases, respec-

tively, which are in good accordance with those for abiotic hydrolysis at pH 5–7 (40–80 days)[20] and aerobic soil metabolism (less 7 days).[11] In the case of **II**, the $T_{1/2}$ values were optimized to be 206 days and 8 days for the water and sediment phases, respectively. The hydrolytic half-life of carbamate is known to be very long,[20] and the transformation half-life of **II** in aerobic soils has been previously reported to be 0.3–6.2 days.[13] These values were close to the optimized $T_{1/2}$ values obtained with TOXSWA. This kinetic analysis showed that the balance between the distribution and degradation profiles in each phase mainly controls the dissipation of **I** and **II** in the water-sediment systems and TOXSWA was found to be more convenient for estimating the dissipation profiles of the pesticide than the compartment model approach.

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