ピリプロキシフェンの光照射下における好気湛水土壌代謝

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Original Article

Effect of illumination on degradation of pyriproxyfen in water-sediment system

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The aerobic aquatic soil metabolism of pyriproxyfen [(4-phenoxyphenyl (*RS*)-2-(2-pyridyloxy) propyl ether] was examined in a UK lake water-sediment system together with the effect of illumination on its degradation profile. The partition of pyriproxyfen in water to the bottom sediment was more rapid under illumination with concomitantly enhanced degradation in the total system. The main photoproduct of pyriproxyfen in sterile water, 2-(pyridin-2-yloxy) propan-1-ol, formed *via* cleavage of the central ether bond, was further degraded *via* oxidation in the illuminated water-sediment system and no degradate was found to be accumulated. Hydroxylation at the 4′-position of the phenoxyphenyl moiety dominantly proceeding in darkness was observed as a transient reaction in the early period of illumination.

Keywords: biodegradation of pesticides, pyriproxyfen, water-sediment system, effect of illumination.

Introduction

Pesticide partly entering the water body *via* spray-drift and run-off events is either partitioned to suspended matter and bottom sediment or degraded by hydrolysis, photolysis and biodegradation.[1] The hydrophobic nature of most pesticides results in their rapid partition to solid surfaces, which generally enables abiotic processes. Some pesticides are known to be susceptible to photolysis, forming a product having a very unique chemical structure *via* bond cleavage and rearrangement[2] and hence, it becomes very important to know the behavior of such a photoproduct in the aquatic environment to assess its impact on various organisms. For this purpose, a laboratory-scale water-sediment study under illumination in addition to the usual study in darkness is required for the European registration of pesticides,[3] as reported for imidacloprid[4] and pyraclostrobin.[5] We have recently investigated the partition and degradation profiles in the illuminated water-sediment system for uniconazole-P[6] and esfenvalerate[7] and demonstrated that the balance between the hydrophobicity controlling the partition to sediment and degradation rate controlling the behavior of these photo-labile pesticides and the contribution of photolysis is greatly reduced. A similar extent of photodegradation was found even in the presence of sediment for chlorothalonil[8], which is less sorptive to soils than our pesticides tested, supporting the above concept.

Pyriproxyfen (**I**, 4-phenoxyphenyl (*RS*)-2-(2-pyridyloxy) propyl ether) is an insecticide developed and used worldwide on apples, tomatoes, cotton and a variety of other crops.[9] **I** is a hydrophobic molecule (log P=5.37) and resistant to hydrolysis under ambient conditions.[10,11] On exposure to UV light (>290 nm) in water at pH 7 and 25°C, **I** degrades with a half-life of 3.7–6.4 days *via* cleavage of each of the three ether linkages in the molecule to form 2-(pyridin-2-yloxy)propan-1-ol as the main photoproduct (70% of the applied dose).[11] Taking account of the profile of **I** and the above considerations, we conducted a water-sediment study of **I** under illumination as well as in darkness to know the effect of illumination on its dissipation profile together with the possible accumulation of the main photoproduct.

Materials and Methods

1. Chemicals

Pyriproxyfen (**I**), uniformly labeled with ^{14}C at the phenoxyphenyl ring [Ph-^{14}C] and at 2,6-positions of the pyridyl ring [Pyr-^{14}C] were synthesized by Amersham Biosciences, UK. The specific activity of each label was 12.4 and 13.0 MBq/mg, respectively, and the radiochemical purity was >99%. The following potential degradates, as shown in Fig.

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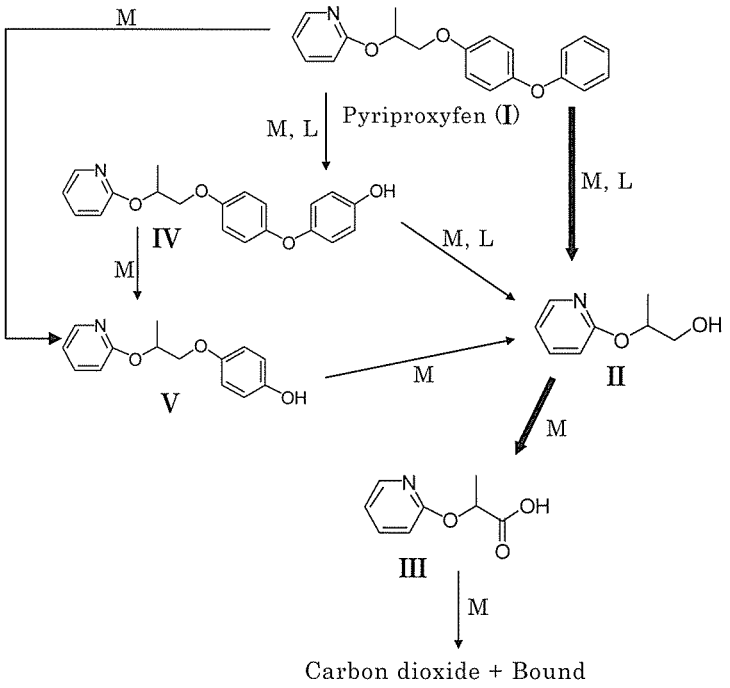

Fig. 1. Proposed degradation pathways of pyriproxyfen (**I**) in water-sediment systems under illumination. M: Microbial, L: Light

1, were synthesized in our laboratory according to the reported methods[12-14]: 2-(pyridin-2-yloxy)-propan-1-ol (**II**), 2-(pyridin-2-yloxy) propanoic acid (**III**), 4-{4-[2-(pyridin-2-yloxy)-propoxy]phenoxy}phenol (**IV**) and 4-[2-(pyridin-2-yloxy)propoxy]phenol (**V**).

2. Radioassay

Radioactivity in water, organic extracts of water and sediment, and trapping media was individually measured by liquid scintillation counting (LSC) with a Packard Tricarb 1900 TR liquid scintillation counter using the liquid scintillation cocktail Starscint™ (Canberra Packard). The unextractable sediment residues were powdered after air-drying at room temperature and a portion was subjected to combustion analysis using a Harvey Biological Sample Oxidizer model OX-300 or 500 with a ^{14}C recovery of >99%. The determination of $^{14}CO_2$ as well as other analytical details was similar to those previously reported.[6,7]

3. Chromatography

Extracts of water and sediment were individually analyzed by reverse-phase high-performance liquid chromatography (HPLC). An ABI Model 759A absorbance detector (Anachem, Bedfordshire, UK) equipped with a Hichron RPB column (5 μm, 4.6-mm i.d.×25 cm) was operated at a flow rate of 1 ml min^{-1} using mobile phase stepwise changing as follows: 0 min, %A (1% acetic acid in water)–%B (acetonitrile), 100:0; 0–5 min, isocratic, 100 : 0 at 5 min; 5–35 min, linear, 0 : 100 at 35 min; 35–45 min, isocratic, 0 : 100 at 45 min; 45–50 min, linear, 100 : 0 at 50 min. The radioactivity of the column effluent was monitored with a β-ram flow through a radioactivity monitor (LabLogic, South Yorkshire, UK) equipped with a 500-μl liquid cell using Quickszint Flow 302 (Zinsser Analytic) as a scintillator. Each ^{14}C peak was identified by HPLC co-chromatography by comparing its retention time with those of non-radiolabeled authentic standards detected by the UV detector at 254 nm. To further confirm the chemical identity of each degradate, thin-layer chromatography (TLC) was conducted using Whatman K6F Silica Gel 60 A plates with a solvent system of toluene/ethyl acetate/acetic acid (70/30/1, v/v/v). Following chromatography, radiolabeled compounds were detected by preparation of a radioautogram of the TLC plate using a BAS 1500 Bio-image analyzer (Fuji Photo Film Co., Ltd.) and non-radiolabeled reference standards were detected by ultraviolet light at 254 nm. Typical HPLC retention times (R_t) in the reverse-phase and TLC R_f values of pyriproxyfen and its potential degradates are listed in Table 1.

4. Metabolism Studies

The water-sediment system used was freshly collected from a lake in Derbyshire, UK. A system with a coarse sediment and relatively low organic carbon content was chosen as the worst-case scenario to minimize the adsorption of **I** to sediment. Water and sediment were passed through 0.2 and 2 mm sieves, respectively. The sediment characteristics are listed in Table 2. The dissolved organic carbon content of the associated water was 7.8 mg C/liter and suspended solids were included in water at 10 mg/liter. The microbial activity in the

Table 1. Chromatographic properties of pyriproxyfen and its potential metabolites

Compound[a]	HPLC Rt (min)[b]	TLC R_f
Pyriproxyfen (**I**)	36	0.65
II	17	0.19
III	19	0.12
IV	31	0.43
V	26	0.39

[a] Corresponding structures are shown in Fig. 1. [b] Typical HPLC retention time.

overlying water was not affected by illumination, as demonstrated by the plate count at the start (1×10^6 colony forming units per ml, cfu/ml) and end of the study (1×10^4 cfu/ml, light; 2×10^4 cfu/ml, dark). After acclimatization for longer than 14 days in the dark and at 20±3°C with complete phase separation, the redox potential of water and sediment were measured as about 500 and 100 mV (hydrogen scale), respectively, and the pH value of each phase was around 7; therefore, the water and sediment layers were in aerobic and rather anaerobic conditions, which well simulated the natural environment.

The vessels used were borosilicate glass cylinders with an internal diameter of 4.5 cm (dark study) and 2.4 cm (illuminated study with dark control) and equipped with side arms. Air was allowed to pass through the vessels to the traps, including ethanediol, 2% paraffin in xylene and 2 M NaOH (× 2), linked in series to collect volatiles. Incubation units contained sediment and associated water at depths of 2.5 and 6 cm in the dark study and 2 and 4 cm in the illuminated study. When the vessels were illuminated, each was individually covered with a quartz lid transparent to the incident light and positioned beneath the filtered xenon arc lamp in Atlas Suntest CPS+. The base of the vessels was enclosed inside a cooling block, cooled by flowing water, and used to maintain the temperature in the units at 20±3°C, similarly to reported previously.[6] The spectral distribution of the incident light (>290 nm) simulated that of natural sunlight and irradiance at 300–800 nm was measured by a LI-1800 spectroradiometer (Li-Cor Inc) to be 343 watts/m^2. Irradiation for 12 hr per day was mostly equal to exposure to summer sunlight.

Table 2. Characteristics of UK lake sediment and associated water samples

Location	Derbyshire, UK
Sediment	
Soil texture (%)[a]	
Sand	66
Silt	12
Clay	22
Soil classification	Sandy clay loam
Organic carbon (%)	3.4
pH (H_2O)	6.1
Associated water	
Dissolved organic carbon (mg C/L)	7.8
Suspended solids (mg/L)	10
pH	6.9

[a] UK particle size distribution

The usual water-sediment study in darkness was conducted for 100 days using [Ph-^{14}C]- and [Pyr-^{14}C]-**I** to examine its distribution and degradation profiles. Each unit was treated with 7 μg of [^{14}C]-**I** in acetonitrile (88 or 92 μl) dropwise injected through a septum-sealed side arm of the vessel. The application rate was calculated from a field application rate of 225 g ai ha^{-1} and assuming an even distribution of **I** to a depth of 30 cm water. The resulting concentration of **I** was below its water solubility (0.37 ppm).[10] The illuminated study with a dark control was similarly conducted using [Pyr-^{14}C]-**I** (1.3 μg/unit with 14 μl acetonitrile) for 30 days to investigate the effect of illumination, especially to know the behavior of **II**, which is known to the main photoproduct in water.

At each sampling, the 0.3-ml aliquot of the overlying water was first removed to measure the dissolved $^{14}CO_2$ by addition to 5 ml of 2 M NaOH. After acidification, the evolved carbon dioxide was trapped in 0.2 M NaOH by passing air through the solution and radioassayed. Secondly, after the direct determination of radioactivity in the overlying water by LSC, the remaining water was acidified to pH 3–4 with acetic acid and extracted three times with 25 ml ethyl acetate. Radioactivity in each phase was radioassayed and the combined organic extracts were subjected to chromatographic analyses. Sediment was extracted three times with 30 ml methanol–water (5 : 1 v/v) followed by acetone–1% acetic acid (5 : 1, v/v). The combined aqueous concentrate was acidified to pH 3–4 and diluted with 15 ml saturated sodium chloride solution. The combined extracts with ethyl acetate (3×25 ml) were concentrated for chromatographic analyses. Selected sediment samples after the above extractions were further extracted by refluxing with acetone–1 M acetic acid (5 : 1 v/v) overnight and the residues were further separated into humin, humic acid and fulvic acid fractions using published methods.[15]

5. *Calculations*

Degradation rates of test compounds and formation fractions of metabolites were calculated using KinGUI software[16] or Excel 2003 (SP3) assuming single first-order kinetics. All degradation rates were determined using SFO kinetics ($y=C_0\times e^{-kt}$), where y is the percent of the test substance at time t days, C_0 is the computed initial percent of the test sub-

stance, and k is the rate constant (slope).

Results

1. *Degradation of* **I** *in the water-sediment in darkness*

The total recovery of radioactivity throughout the study was 90.2–98.6% of the applied ^{14}C for both labels. Aqueous ^{14}C rapidly decreased to less than 40% after 2 days by partitioning to the bottom sediment. The amount of bound ^{14}C increased with incubation to 51.4% ([Ph-^{14}C]) and 30.9% ([Pyr-^{14}C]) after 100 days. Reflux extraction under acidic conditions released only 3–5% of the applied ^{14}C from each label and the residual ^{14}C was fractionated into humin (13.1–22.7%), humic acid (4.4–8.3%) and fulvic acid (9.9–16.2%). No volatile ^{14}C was collected in organic traps but $^{14}CO_2$ was gradually generated, finally to 11.0–24.6% of the applied ^{14}C to a less extent from [Pyr-^{14}C]-**I**, as shown Tables 3 and 4. HPLC analysis of the extracts from each phase showed differences in the distribution of **I** between the labels, most likely due to the heterogeneity of the water-sediment system. Based on single first-order kinetics, DT_{50} and DT_{90} values of **I** in the total system were estimated to be 8.0–10.5 and 27–35 days (r^2= 0.903–0.938), respectively.

One of the common metabolites to both labels was **IV**, which after 14–50 days was 4.8–11.7% and 8.4–9.2% for [Ph-^{14}C]- and [Pyr-^{14}C]-**I**, respectively, and was dominantly detected in the sediment phase. The other common metabolite was **V**, which sporadically reached 11.8% in the water phase of [Ph-^{14}C]-**I** after 2 days but mostly stayed at 1–4 % in total throughout the study. **III** was detected as a major metabolite specific to [Pyr-^{14}C]-**I** with the maximum amount of 31.2% of the applied ^{14}C after 100 days, most of which was present in the water phase (23.6%). Since **III** is a carboxylic acid derivative, its predominance in water is most likely. Cleavage of the central ether linkage is considered to form **II** and 4-phenoxyphenol, but **II** was a minor metabolite at 0.3–0.8% in water, and the latter phenol originating from [Ph-^{14}C]-**I** was not detected; therefore, **II** was considered to be rapidly oxidized to **III**. Since there were no major unique metabolites amounting to >1% formed from [Ph-^{14}C]-**I**, the phenol derivative was likely to be bound to sediment or mineralized. Based on these results, **I** was considered to be moderately partitioned to the sediment phase with concomitant degradation mainly *via* hydrolxylation at 4′-position of the phenoxyphenyl moiety to form **IV** or cleavage of the central ether linkage followed by rapid oxidation to form **III**. Either the ether cleavage at the phenoxy moiety of **I** or successive degradation of **IV** was considered to form **V** but to a lesser extent. These metabolites underwent further degradation followed by binding to sediment and mineralization.

2. *Degradation of* **I** *in the illuminated system*

The good ^{14}C recovery of 89.5–102.9% was observed similarly to the dark study in a larger vessel, as shown in Tables 5 and 6. The partition of ^{14}C to sediment was more rapid under

Table 3. Distribution of [Ph-^{14}C]-**I** and its degradates in UK usual water-sediment system under dark conditions

	% of the applied radioactivity							
	0 d[a)]	1 d	2 d	3 d	7 d	14 d	50 d	100d
Volatile	—[b)]	0.1	1.3	1.9	2.7	4.4	14.2	24.7
CO_2	—	0.1	1.3	1.9	2.7	4.4	14.1	24.6
Water phase	73.1	40.8	33.5	13.3	20.8	14.9	7.1	2.7
Pyriproxyfen (**I**)	72.2	39.5	12.4	9.5	14.8	3.1	0.2	n.d.
IV	n.d.[c)]	0.7	3.0	1.0	1.9	1.9	n.d.	n.d.
V	n.d.	n.d.	11.8	n.d.	0.9	4.4	0.8	n.d.
Others	0.9	0.6	6.3	2.8	3.2	5.5	6.1	2.7
Sediment phase	24.7	54.3	55.2	74.7	67.5	72.6	70.2	62.2
Extract	24.6	46.5	28.0	45.3	47.1	43.2	22.9	10.8
Pyriproxyfen (**I**)	23.8	44.7	24.9	39.9	*[d)]	30.2	13.5	5.7
IV	n.d.	n.d.	1.0	2.2	*	9.8	4.8	2.3
V	n.d.	n.d.	0.9	n.d.	*	3.1	3.2	2.2
Others	0.8	1.8	1.2	3.2	*	0.1	1.4	0.6
Bound residues	0.1	7.8	27.2	29.4	20.4	29.4	47.3	51.4
Unit rinses	—	0.8	1.7	0.3	0.8	2.4	0.5	1.0
Total	97.8	96.0	91.7	90.2	91.8	94.3	92.0	90.6

[a)] d: day(s), [b)] —: not analyzed. [c)] n.d.: not detected. [d)]*: data not used due to failed work-up.

Table 4. Distribution of [Pyr-^{14}C]-**I** and its degradates in UK usual water-sediment system under dark conditions

	% of the applied radioactivity							
	0 d[a]	1 d	2 d	3 d	7 d	14 d	50 d	100d
Volatile	—[b]	n.d.	0.1	0.8	1.3	2.2	6.2	11.0
CO_2	—	n.d.	0.1	0.8	1.3	2.2	6.2	11.0
Water phase	74.8	59.8	38.6	36.4	27.7	22.1	25.8	26.9
Pyriproxyfen (**I**)	74.3	55.4	29.9	20.7	11.9	1.7	n.d.	n.d.
III	n.d.[c]	2.5	6.7	10.1	12.4	13.5	19.4	23.6
IV	n.d.	0.9	0.5	1.1	n.d.	1.4	n.d.	n.d.
V	n.d.	n.d.	n.d.	0.9	n.d.	1.4	n.d.	n.d.
Others	0.5	1.0	1.5	3.6	3.4	4.1	6.4	3.3
Sediment phase	23.8	34.9	57.1	57.2	65.9	69.4	61.2	53.9
Extract	23.7	31.6	50.1	43.9	52.1	50.0	33.5	23.0
Pyriproxyfen (I)	22.5	30.6	46.2	38.4	43.6	35.8	13.5	9.2
III	n.d.	n.d.	n.d.	1.2	2.5	4.1	6.2	7.6
IV	n.d.	n.d.	1.3	3.1	4.7	7.0	9.2	3.3
V	n.d.	n.d.	n.d.	n.d.	0.8	2.0	2.9	1.8
Others	1.2	1.0	2.6	1.2	0.5	1.1	1.7	1.1
Bound residues	0.1	3.3	7.0	13.3	13.8	19.4	27.7	30.9
Unit rinses	—	0.9	0.5	0.5	2.2	2.3	0.1	0.8
Total	98.6	95.6	96.3	94.9	97.1	96.0	93.3	92.6

[a] d: day(s), [b] —: not analyzed. [c] n.d.: not detected.

Table 5. Distribution of [Pyr-^{14}C]-**I** and its degradates in UK water-sediment system under illumination

	% of the applied radioactivity						
	0 d[a]	1 d	2 d	3 d	7 d	14 d	30 d
Volatile	—[b]	0.1	0.2	0.8	3.7	4.9	9.4
CO_2	—	0.1	0.2	0.8	3.7	4.9	9.2
Water phase	46.9	26.8	25.1	24.4	28.4	29.3	11.1
Pyriproxyfen (**I**)	46.8	22.0	15.0	7.6	n.d.	n.d.	n.d.
II	n.d.[c]	1.5	2.1	2.7	0.2	n.d.	n.d.
III	n.d.	1.3	3.7	8.9	21.5	25.3	9.5
IV	n.d.	0.7	0.7	n.d.	n.d.	n.d.	n.d.
V	n.d.	n.d.	0.5	1.3	0.9	n.d.	n.d.
Others	0.1	1.3	3.1	3.9	5.8	4.0	1.6
Sediment phase	50.5	69.5	70.6	70.5	61.3	59.4	67.0
Extract	50.3	64.3	57.7	51.2	24.7	20.5	21.6
Pyriproxyfen (**I**)	49.1	52.8	37.5	42.2	14.1	2.9	14.2
II	n.d.	n.d.	0.2	n.d.	n.d.	n.d.	n.d.
III	n.d.	0.3	0.8	n.d.	8.9	13.4	5.4
IV	n.d.	9.3	16.1	8.2	n.d.	0.9	n.d.
V	n.d.	0.4	2.5	n.d.	n.d.	1.4	n.d.
Others	1.2	1.5	0.6	0.8	1.7	1.9	2.0
Bound residues	0.2	5.2	12.9	19.3	36.6	38.9	45.4
Total	97.4	96.4	95.9	95.7	93.4	93.6	89.5[d]

[a] d: day(s), [b] —: not analyzed. [c] n.d.: not detected., [d] Including the additional radioactivity recovered by unit soaking and tubing washing.

Table 6. Distribution of [Pyr-^{14}C]-**I** and its degradates in UK water-sediment system (dark control)

	% of the applied radioactivity						
	0 d[a]	1 d	2 d	3 d	7 d	14 d	30 d
Volatile	—[b]	—	n.d.	0.1	0.1	0.9	1.6
CO_2	—	—	n.d.	0.1	0.1	0.9	1.6
Water phase	53.1	56.0	59.0	43.8	37.3	14.3	8.5
Pyriproxyfen (**I**)	52.9	54.3	56.6	37.2	29.4	5.3	0.9
II	n.d.[c]	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
III	n.d.	n.d.	n.d.	0.8	2.4	6.5	4.4
IV	n.d.	1.0	1.5	3.1	2.6	0.7	0.2
V	n.d.	n.d.	n.d.	n.d.	n.d.	0.4	1.3
Others	0.2	0.7	0.9	2.7	2.9	1.4	1.7
Sediment phase	46.0	46.9	39.3	53.4	57.6	80.2	78.6
Extract	45.8	45.4	38.1	51.7	52.8	69.3	68.4
Pyriproxyfen (**I**)	44.8	39.1	35.3	48.8	47.8	57.1	50.2
II	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
III	n.d.	n.d.	n.d.	n.d.	n.d.	1.8	0.6
IV	n.d.	1.3	1.7	n.d.	4.1	6.8	11.0
V	n.d.	n.d.	n.d.	n.d.	n.d.	0.6	4.3
Others	1.0	5.0	1.1	2.9	0.9	3.0	2.3
Bound residues	0.2	1.5	1.2	1.7	4.8	10.9	10.2
Total	99.1	102.9	98.3	97.3	95.0	95.4	90.5[d]

[a] d: day(s), [b] — : not analyzed. [c] n.d.: not detected. [d] Including the additional radioactivity recovered by unit soaking and tubing washing.

illumination than in the dark control but the final distribution between water and sediment phases was similar. Although a simple comparison could not be conducted due to the different incubation times, the levels of $^{14}CO_2$ were similar in the dark studies between the larger (2.2% at day-14) and smaller (1.6% at day-30) vessels but the formation of bound residues was greater in the larger vessels (19.4% at day-14 and 10.2% at day-30). In contrast, the formation of $^{14}CO_2$ and bound residues was greatly enhanced under illumination by a factor of 4–6, indicating intensive photodegradation with mineralization. More distribution of ^{14}C in the fraction of humin (16.5%) and fulvic acids (15.3%) than that of humic acids (7.3%) after 30 days was observed similarly to the dark study in the larger vessels.

The dissipation of **I** in the total system in the dark control was slower in the smaller vessels (DT_{50}=29 days, r^2=0.957) than the larger vessels (10.5 days), possibly due to the different population of microorganisms considering the almost constant distribution of **I** in the sediment of the smaller vessels during the study. The metabolic profiles of **I** in the dark control of illumination were very similar to those in the larger vessels. The main metabolite was **IV**, amounting to 11.2% of the applied ^{14}C after 30 days, most of which was detected in sediment. The other metabolites were **III** and **V** at around 5%. In contrast, illumination not only greatly accelerated its dissipation with a DT_{50} value of 3 days but also modified the degradation profile, as shown in Fig. 2. The earlier formation of **IV** was observed with a maximum of 16.8% after 2 days, followed by rapid dissipation to the non-detection level after 7 days. Slightly less **V** was detected throughout the study as compared with the dark control. The most different profile was the greater formation of **III** with a maximum of 38.7% after 14 days, together with the detection of **II** at trace levels (0.2–2.7% before 7 days). Although detailed kinetic analysis was not conducted, the DT_{50} value of **III** in the total water-sediment system should be less than 2 weeks from its dissipation to 14.9% after 30 days. Based on these results, **I** was considered to be more rapidly dissipated under illumination and the main product **II** in the photodegradation of **I** in sterile buffer at pH 7[11] was unlikely to be accumulated.

Discussion

Microbial degradation of **I** *via* hydroxylation at the terminal phenyl ring and ether cleavage was most likely in the water-sediment system, as previously reported for many pesticides.[1] Similar metabolites have been reported through the aerobic soil metabolism of fenvalerate.[17] Furthermore, oxidases are likely to be involved in this transformation, which was sup-

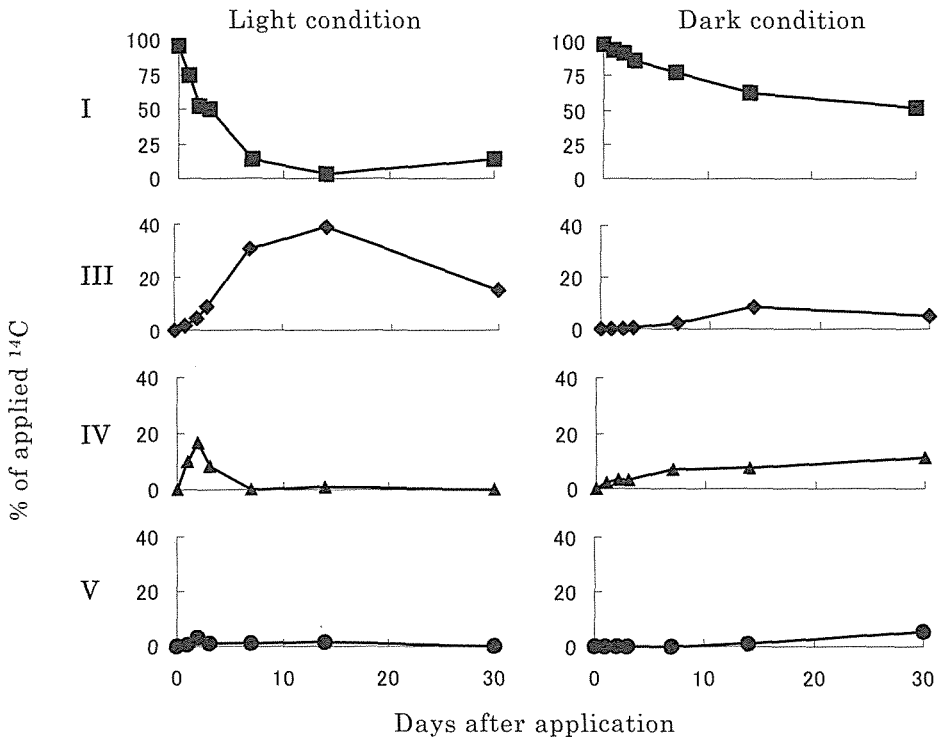

Fig. 2. *Dissipation of pyriproxyfen (**I**) and formation of its metabolites in a water-sediment system in the light (left) and dark (right).*

ported by the iron-porphyrin catalyzed oxidation of **I**. Fukushima *et al.*[18] examined the chemical oxidation of **I** using iron porphyrin as an analogue of cytochrome P450 in the presence of hydrogen peroxide and found that the main metabolites are **II**, **IV** and **V**. In the water-sediment system, **III** was detected as a major metabolite instead of **II** and this difference may originate from the lower activity of the chemical oxidation utilized for aliphatic alcohols than aromatic rings.[19] The mineralization from [Pyr-^{14}C]-**I** but to a less extent than that from [Ph-^{14}C]-**I** indicated possible ring opening during microbial metabolism as similarly reported for nitrogen heterocycles.[20]

Since the photolysis of [Pyr-^{14}C]-**I** in sterile water at pH 7 produced **II** as a single identified product and **I** has an absorption maximum in water at 270 nm with its shoulder extending above 300 nm,[10,11] direct photolysis is considered to be predominant. The highest occupied molecular orbital of **I** is localized at the aromatic carbons attaching to the ether oxygen atoms[18] and electron excitation to higher unoccupied energy levels are most likely to weaken ether bonds, which may result in the formation of **II**. The presence of **IV** and **V** in the illuminated water-sediment indicates the involvement of an indirect photolytic process. Humic substances and clay particles are known to produce active oxygen species such as hydroxyl radical.[2,21] In the case of the photodegradation of esfenvalerate, the presence of humic acids and clay minerals has been reported to cause either hydroxylation at the 4′-position of the 3-phenoxybenzyl moiety or cleavage of the ether bond connecting two phenyl rings;[22,23] therefore, a similar mechanism is likely to occur in the illuminated water-sediment, leading to the formation of **IV** and **V**. **III** would be quickly formed from **II**, since the photo-induced oxidation of alcohol to the corresponding acid is a well-known pathway.[2] Irrespective of the photolytic mechanism involved, these degradates can be formed much earlier by photolysis than microbial metabolism, which is in accordance with the formation profile of **IV**. The detection of **II** in trace amounts during the study but with a greater formation of **III** suggests that **II** is immediately degraded *via* either photo-induced or microbial oxidation. The illumination accelerated the dissipation of **I** from the water phase with DT_{50} values from 6 days to 1 day by its photodegradation and distribution to the sediment phase. Considering the lack of increase of **I** in the sediment phase by accelerated dissipation from the water phase and formation of **IV** and bound residues, **I** degraded in the sediment phase and this occurred by illumination. Generally, the contribution of photolysis was reduced by the existing sediment phase with adsorption or diffusion to the lower layer, and the observation showed that photoinduced degradation might occur on the sediment surface. The rapid partition of **I** from water to sediment due to its partition coefficient (Koc) to sediment of 4980 kg^{-1} of organic carbon[10] showed the possible photodegradation of **I** on the illuminated sediment surface as well as in the water phase. **III**, **IV** and **V** were then partitioned to either phase depending on their Koc. The Koc values of **III** and **IV** are 120 and 2757 in sediment,[10] which could account for

their favorable distribution in water and sediment, respectively. Although the Koc value of **V** was not available, the EPI-Suite program[24] estimated a smaller value than that of **I** by an order, which explained the fluctuating distribution of **V** between two phases in the larger vessels in darkness.

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ピリプロキシフェンの光照射下における好気湛水土壌代謝

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ピリプロキシフェンの好気湛水土壌代謝に光照射が及ぼす影響について英国の湖水－底質系を用いて調べた．ピリプロキシフェンの底質への分配および分解は光照射により促進された．光照射下の好気湛水土壌中では蓄積傾向を示す代謝分解物は認められず，エーテル結合の開裂により生じ，滅菌水中の主要な光分解物として報告されている 2-(pyridin-2-yloxy)propan-1-ol は速やかに酸化された．暗条件下の好気湛水土壌系における主要な代謝分解経路であるフェノキシフェニル基の 4′ 位の水酸化は光照射下では初期に一過性で認められたのみであった．