Photodegradation of Fenvalerate (Sumicidin®) in Water and on Soil Surface

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On exposure to sunlight, fenvalerate [α -cyano-3-phenoxybenzyl-2-(4-chlorophenyl) isovalerate] was rapidly decomposed in distilled water, 2% aqueous acetone, river and sea water to almost the same extent. The half-life of fenvalerate photodegradation in each aqueous suspension ranged from ca. 4 days in summer to 13–15 days in winter, due to seasonal variation of sunlight intensity. The quantum yield was determined to be 6.8×10^{-3} (at 313 nm in water), and the half-life of disappearance at 40 degree North Latitude was calculated to be 4.1 days and 12.4 days in summer and in winter, respectively. On soil surface, the rate of photodegradation was different depending on the soil used, with half-lives of approximately 2, 6 and 18 days in Kodaira light clay, Azuchi sandy clay loam and Katano sandy loam soils, respectively. Without sunlight, approximately 55 to 83% of the applied fenvalerate remained on these soils 20 days post-treatment. Fenvalerate was photodecomposed by oxidation, decarboxylation, hydration at CN group to CONH₂, cleavage of ester or diphenyl ether linkage, hydrolysis from CONH₂ to COOH. Hydrogen cyanide was also liberated in water and promptly transformed to carbon dioxide by natural sunlight. The predominant reactions were decarboxylation and cleavage of ester linkage in water, whereas hydration at CN group was dominant on soil surface. Thus, photodegradation rates and pathways for fenvalerate were somewhat dependent on the environmental conditions tested.

INTRODUCTION

Fenvalerate [Sumicidin®, α -cyano-3-phenoxybenzyl-2-(4-chlorophenyl) isovalerate] is now under rapid development as an agricultural insecticide, because it possesses high insecticidal activity toward a wide range of insect pests,¹⁾ moderate mammalian toxicity²⁾ and adequate stability in the field.^{3,4)} In connection with practical usage of this chemical in agriculture, photolysis studies of fenvalerate were conducted with a view to having deeper understanding of the environmental fate of this compound.

Holmsted *et al.* investigated the photochemical reactions of fenvalerate, especially in various organic solvents by UV light.^{5,6)} However, these data are insufficient to estimate the photochemical behavior of this compound in the environment.

This paper deals with degradation rates and

pathways for ¹⁴CN-, ¹⁴CO- and ¹⁴C α -fenvalerate in distilled water, 2% aqueous acetone, river and sea water as well as on three types of soil under natural sunlight. The direct photolysis half-life of fenvalerate in water was also calculated as a function of season, latitude and depth of water by a recently published technique.⁷⁾

MATERIALS AND METHODS

1. Chemicals

Three ¹⁴C-labeled preparation of fenvalerate were synthesized in the Institute for Biological Science, Sumitomo Chemical Co., Ltd.⁸⁾ ¹⁴CO-[2RS, α RS]-fenvalerate labeled at CO group was the ester of ($\pm$)-2-(4-chlorophenyl) isovaleric acid and ($\pm$)-3-phenoxybenzylcyanohydrin. ¹⁴C α -[2S, α RS]- and ¹⁴CN-[2S, α RS]-fenvalerate labeled at CH in the benzyl group and CN, respectively, were the ester of (+)-2-(4-chlorophenyl) isovaleric acid and ($\pm$)-3-

phenoxybenzylcyanohydrin. The specific activity was as follows: ^{14}C -fenvalerate, 4.75 mCi/mmol; ^{14}CN -fenvalerate, 15.7 mCi/mmol; $^{14}\text{C}\alpha$ -fenvalerate, 20 mCi/mmol. Each preparation had a radiochemical purity of more than 99% based on thin-layer chromatography, radioautography and liquid scintillation counting.

^{14}C -Parathion, uniformly labeled in the phenyl ring, was prepared as a reference compound for determination of quantum yield.⁹⁾ The specific activity was 3.99 mCi/mmol with the purity of more than 99% both radiochemically and chemically.

The following unlabeled compounds were prepared in this laboratory for reference:^{3,6)} 2-(4-chlorophenyl) isovaleric acid [Cl-Vacid], 3-phenoxybenzyl alcohol [PBalc], 3-phenoxybenzaldehyde [PBald], α -carbamoyl-3-phenoxybenzyl-2-(4-chlorophenyl) isovalerate [CONH_2 -fenvalerate], α -carbamoyl-3-hydroxybenzyl-2-(4-chlorophenyl) isovalerate [CONH_2 -desphenylfenvalerate], 3-phenoxybenzyl cyanide [PBCN], 3-phenoxyphenyl acetic acid [PPA], 3-phenoxyphenyl acetamide [CONH_2 -PPA], α -carboxy-3-phenoxybenzyl-2-(4-chlorophenyl) isovalerate [COOH -fenvalerate], 2-(3-phenoxyphenyl)-3-(4-chlorophenyl)-4-methyl pentanenitrile [decarboxy-fenvalerate].

2. Radioassay

The radiocarbon contents of gel regions from *tlc* plates and organosoluble fractions from extraction of water, soil and polyurethane plug were determined in a low potassium glass vial with a model 3385 liquid scintillation spectrometer (Packard), using 10 ml of a dioxane scintillation fluid (5 g of 2,5-diphenyl-oxazole and 100 g of naphthalene in 1 liter of dioxane). Each sample was counted with a preset time of 5 min. Liquid scintillation counting (*lsc*) data were corrected for counting efficiency and background levels. Counting efficiency and background levels were more than 85% and 38 ± 7.5 dpm, respectively. For determination of ^{14}C in acidic and alkaline solutions as well as river and sea water, Aquasol®-2 (New England Nuclear) was utilized. After 10 ml of each solution was mixed well with the same volume of Aquasol®-2 in a glass vial, it was kept at 4°C for 8 hr prior to *lsc*. In this case, counting efficiency was approximately 75% and background levels ranged from 50 to 60 dpm. The unextractable soil residues were dried over P_2O_5 in a vacuum desiccator, powdered, sampled in duplicate (300 mg) and then combusted with a model 306 sample oxidizer (Packard) prior to *lsc*. More than 90% of radiocarbon was recovered in a mixture of Oxisorb®- CO_2 absorber (New

Table 1 Thin-layer chromatographic properties of fenvalerate and its degradation products.

Compound	<i>Rf</i> values with indicated solvent systems ^{a)}			
	A	B	C	D × 6
Fenvalerate	0.86	0.65	0.60	0.31, 0.36
Decarboxy-Fen	0.83	0.64	0.59	0.27, 0.40
CONH_2 -Fen	0.26, 0.29	0.23, 0.26	0.29, 0.32	0.02, 0.04
CONH_2 -Desphenyl fen	0.15	0.05	0.10	0
COOH -Fen	0.52	0.28	0.36	0
PBCN	0.73	0.56	0.49	0.20
CONH_2 -PPA	0.16	0.13	0.20	
PPA	0.41	0.31	0.36	0
Cl-Vacid	0.54	0.44	0.45	0.07
PBalc	0.43	0.35	0.28	0.05
PBald	0.77	0.56	0.52	0.52
PBacid	0.46	0.40	0.41	0.02

a) A: benzene saturated with formic acid/ether (10/3)

B: *n*-hexane/toluene/acetic acid (3/15/2)

C: toluene/acetic acid (7/1)

D: *n*-hexane/ether (20/1)

England Nuclear) and 15 ml of Oxiprep®-2 oxidizer scintillator (New England Nuclear). Counting efficiency was approximately 75% and background levels were 66 ± 12 dpm.

3. Thin-layer Chromatography (tlc)

Precoated silica gel 60F-254 chromatoplates (20×20 cm, 0.25 mm layer thickness, E. Merck) were used for analytical and preparative purposes in the following solvent systems: A) benzene saturated with formic acid/ ether (10/3); B) *n*-hexane/toluene/acetic acid (3/15/2); C) toluene/acetic acid (7/1); D) *n*-hexane/ether (20/1). The *R_f* values for fenvalerate and its photoproducts are given in Table I. The solvent system designated as (D $\times$ 6) indicates the development with solvent system D for 6 times. The photoproducts were tentatively identified by *tlc* cochromatography with the unlabeled standard. The resolved radioactive spots were detected by radioautography with the developed *tlc* plates held under the X-ray N-150 film (Fuji Photo Film) at 4°C for 7 or 14 days and the non-radioactive compounds were detected by ultraviolet fluorescence quenching. Quantitation of radiocarbon was conducted by scraping the radioactive gel regions into glass vials and counting them. The radioactive spots with more than 150 dpm were quantitatively determined in the procedure described above.

4. Photolysis in Water

In addition to distilled water, 2% aqueous acetone solution as well as natural water from river and sea was utilized in the photolysis experiments. The natural water was collected from Muko River (pH 7.8) or Nishinomiya Seaside (pH 8.0) in Hyogo Prefecture. These water samples were filter-sterilized by passage through a 0.1 μ m Millipore filter immediately before use. Because of rapid disappearance of fenvalerate in each water solution even below its solubility (50–200 ppb), probably due to adsorption to glass wall, more stable suspension of ^{14}C -fenvalerate at 50 ppb was prepared using as an emulsifier Tween 85 with no UV absorption above 290 nm. The preparation of ^{14}C -fenvalerate suspension was as follows: ^{14}C -fenvalerate (400 μ g) and Tween 85 (20 mg) were dissolved in 10 ml of methanol and 1 ml

of the solution was taken into a 1-liter quartz flask. After evaporation of solvent by nitrogen gas, 800 ml of water was added and then stirred by a mechanical shaker for 1 hr to attain a level of 50 ppb. More than 90% of radioactivity was recovered from aqueous suspension of fenvalerate after standing for 10 days without stirring. Each of these flasks was exposed to natural sunlight for 6 weeks (10 hr per day from July to August in 1978 in the case of ^{14}CN -fenvalerate or 8 hr per day from January to February in 1979 for ^{14}CO - or $^{14}\text{C}\alpha$ -fenvalerate) at Takarazuka, Hyogo, Japan. Sunlight intensity with wavelength between 300 and 400 nm was approximately 530, 1730 and 210 $\mu\text{W}/\text{cm}^2$ (from July to August) and 100, 420 and 130 $\mu\text{W}/\text{cm}^2$ (from January to February) at the beginning, middle and end of the day, respectively. During exposure to sunlight, carbon dioxide-free air was continuously supplied over the water surface at 100 ml/min and the effluent air was passed serially through a polyurethane form plug and gas-washing bottles containing 400 ml of 0.5 N NaOH solution to trap volatile ^{14}C including $^{14}\text{CO}_2$ and H^{14}CN . A dark control experiment was also conducted by covering the flask with aluminum foil to ensure that a given product was derived from photochemical processes.

5. Extraction Procedures

At 1, 2, 4 and 6 weeks after irradiation, the polyurethane plug was removed and eluted three times with 50 ml of methanol. An aliquot of the fenvalerate suspension was taken from each flask into a gas-washing bottle and acidified to pH 2 with 2 N sulfuric acid to determine the content of $^{14}\text{CO}_2$ and/or H^{14}CN in each suspension prior to being subjected to extraction three times with two fold volumes of ethyl acetate. By bubbling of nitrogen gas into each acidified suspension at 1,500 ml/min for 30 min, $^{14}\text{CO}_2$ and/or H^{14}CN were trapped in 0.5 N NaOH solution. Recovery of each product exceeded 90%. After precipitation of $^{14}\text{CO}_2$ as $\text{Ba}^{14}\text{CO}_3$ by addition of 2 N BaCl_2 followed by centrifugation, the supernatant was readjusted to pH 3, through which helium gas was bubbled at a rate of 100 ml/min for 6 hr to trap the liberated H^{14}CN in a glass tube in liquid nitrogen. The hydrogen cyanide

trapped in the glass tube was dissolved in 2 ml of 0.1 N NaOH and 0.5 ml of the solution was subjected directly to colorimetric analysis.¹⁰⁾ More than 80% of hydrogen cyanide with the amounts ranging from 4 ng to 100 ng was recovered. Radioactive carbon dioxide and H^{14}CN in alkaline trap serially connected with the photoreaction bottle were both qualitatively and quantitatively determined by the same procedure as described above.

Each combined solvent extract of polyurethane plug or aqueous suspension was radioassayed by *lsc* and then evaporated to dryness. The residue was dissolved in a small volume of methanol, an aliquot of which was subjected to silica gel *tlc* with solvent systems A, B, C or (D×6).

6. Photolysis on Soil Surface

As soil sources, Kodaira light clay (Tokyo Metropolis), Katano sandy loam (Hyogo Pref.) and Azuchi sandy clay loam (Shiga Pref.) were used, whose characteristics are described in Table 2. The soil thin layer plates (10×10 cm, 500 μm thickness) were prepared with fine particles of the soil passed through 2 mm sieve, according to the method of Helling *et al.*¹¹⁾ Onto each soil *tlc* plate, one ml of $^{14}\text{C}\alpha$ - or ^{14}CN -fenvalerate in ether was evenly applied with a brush to give a concentration of 0.55–0.59 $\mu\text{g}/\text{cm}^2$ and then exposed to natural sunlight during September in 1978, in Takarazuka, Hyogo, Japan. During the photolysis, the water content of Kodaira, Katano and Azuchi soil *tlc* plates changed from 12 to 1.6, 4 to 0.6 and 5 to 0.8%, respectively. As a dark control, soil *tlc* plates were held in the dark.

7. Extraction Procedures

At specified intervals, each soil thin layer was scraped from the glass plate and extracted three times with 30 ml of methanol/water (5/1) mixture by shaking. The combined extract was monitored for ^{14}C and concentrated to dryness in a rotary vacuum evaporator. The residue was dissolved in a certain volume of methanol, an aliquot of which was subjected to *tlc* with solvent systems A, B and (D×6). Immediately after application of ^{14}C -fenvalerate to soil *tlc* plates, more than 95% of the radiocarbon was recovered through extraction, *tlc* and *lsc* procedures.

8. Determination of Direct Photolysis Rates

The direct photolysis rates of fenvalerate in aqueous suspension at shallow depth was calculated as a function of season and latitude by Eq. 1, assuming that the rate obeys a first-order kinetics,

$$-\left(\frac{d[P]}{dt}\right)_i = \phi_i k_{ai} [P] \quad (1)$$

Where ϕ_i is the quantum yield and k_{ai} is the specific sunlight absorption rates, respectively. Since the quantum yield (ϕ_i) is generally wavelength-independent in solution according to Vavilov's law except for certain coordination compounds,¹²⁾ the complete rate is expressed by Eq. 2.

$$-\left(\frac{d[P]}{dt}\right) = \phi k_a [P] \quad (2)$$

According to Eq. 2, the half-life ($T_{1/2}$) of decomposition is given by Eq. 3.

$$T_{1/2} = \frac{0.693}{\phi k_a} \quad (3)$$

The quantum yield of disappearance can be calculated by Eq. 4,

Table 2 Physico-chemical characteristics of soils used in the experiment.

Sampling site	Soil texture	pH	Soil separate (%)			Clay mineral	O.M. ^{a)}	C.E.C ^{b)}	Maximum water-holding capacity ^{c)}
			Sand	Silt	Clay				
Kodaira	Light clay	5.5	31	40	29	Kaolinite	15.3	53.7	148.5
Katano	Sandy loam	4.6	90	2	8	Kaolinite	1.9	9.3	79.6
Azuchi	Sandy clay loam	6.3	65	18	17	Allophane	2.5	13.5	88.7

^{a)} organic matter contents (%), ^{b)} cation exchange capacity (meq/100 g dry soil),

^{c)} g/100 g dry soil.

$$\phi = \frac{\Delta P}{\Delta R} \frac{\epsilon R \cdot \phi R}{\epsilon P} \quad (4)$$

where ΔP and ΔR are the slopes of log plots of concentration vs. exposure time for the tested compound and the reference compound, respectively; ϵR and ϵP are molar extinction coefficients of reference and tested compound, respectively; ϕR is the quantum yield for reference compound. The value of $\epsilon R \cdot \phi R$ at 313 nm for parathion in water is 0.39.¹³⁾

Specific rates of sunlight absorption k_a equals $\Sigma k_{a,i}$, the sum of the $k_{a,i}$ values for all wavelengths of sunlight that are absorbed by fenvalerate.

9. Measurement of Quantum Yields

The quantum yield of fenvalerate was determined by comparing the photolysis rate with that of parathion as a reference compound at 313 nm by using a merry-go-round type photochemical apparatus which allowed to achieve equal irradiation of all reaction tubes. To obtain monochromatic light with the wavelength of 313 nm, the light derived from 450-W medium pressure mercury vapor lamp (Taika Kogyo Co., Ltd.) was filtered through 1-cm thick solution of 0.001 M potassium chromate in 3% aqueous potassium carbonate,¹⁴⁾ followed by UV-D35 glass filter (Toshiba Electric Co., Ltd.).

Each seven milliliters of aqueous suspension of $^{14}\text{C}\alpha$ -fenvalerate at 50 ppb, prepared in the same way as described above, and aqueous solution of ^{14}C -parathion at 200 ppb was placed in a quartz tube of the apparatus, and irradiated up to 12 hr at 313 nm. The tubes were withdrawn at specified intervals and the solution was analyzed for the present compound as follows: $^{14}\text{C}\alpha$ -fenvalerate and ^{14}C -parathion were extracted three times with two-fold volumes of ethyl acetate and dichloromethane, respectively. The organic layer was concentrated to dryness and an aliquot of the residue dissolved in a small volume of acetone was subjected to *tlc* with the solvent system (D $\times$ 6) for fenvalerate and the solvent system C for parathion.

10. Calculation of Specific Rates of Sunlight Absorption

Specific rates of sunlight absorption, k_a ,

were calculated according to Eq. 5,

$$k_a = \frac{1}{D} \sum [I_{d,i}(1 - 10^{-\alpha_i l_d}) + I_{s,i}(1 - 10^{-\alpha_i l_s})] \epsilon_i \alpha_i^{-1} \quad (5)$$

where D is the depth of water; $I_{d,i}$ and $I_{s,i}$ are intensities of vertical component of sun radiation and sky radiation, respectively; α_i is the decadic absorption coefficient of water; ϵ_i is the molecular extinction coefficient of the pesticide; l_d and l_s are pathlengths for sun radiation and sky radiation in water, respectively.

Near the surface of water layer, k_a becomes independent of α_i and can be expressed by Eq. 6.

$$k_a = \frac{2.303}{D} \sum \epsilon_i (I_{d,i} l_d + I_{s,i} l_s) J^{-1} \quad (6)$$

The conversion constant, J , equals 6.02×10^{20} when concentration of pesticide is expressed in mole/liter and sunlight intensity in photons $\text{cm}^{-2}\text{s}^{-1}$.

The pathlength l_d and l_s can be expressed by Eq. 7 and 8, respectively,

$$l_d = nD / \sqrt{n^2 - \sin^2 z} \quad (7)$$

$$l_s = 2nD / (n - \sqrt{n^2 - 1}) \quad (8)$$

where n is a refractive index of water and z is the solar zenith angle. Assuming the refractive index, n , of water is 1.34, the computed pathlength l_d is $1.2D$. More detailed derivation of the Eqs. 1–8 was published elsewhere⁷⁾.

The values of $I_{d,i}$ and $I_{s,i}$ were taken from a report published by Bener.¹⁵⁾

As the absorption spectrum of fenvalerate was the same in ethanol as in aqueous suspension in Tween 85, the exact molar extinction coefficient of fenvalerate was measured by using concentrated (25 ppm) ethanol solution.

RESULTS

On exposure to sunlight, ^{14}CN -fenvalerate was degraded promptly with almost the same rate with a half-life of approximately 4 days in each aqueous suspension, as shown in Fig. 1. Accompanied with breakdown of fenvalerate, the amounts of $^{14}\text{CO}_2$ rather than H^{14}CN increased, except in 2% aqueous acetone. Especially in distilled and sea water, $^{14}\text{CO}_2$ accounted for approximately 55% after 6-

Fig. 1 Degradation of ^{14}C -(2S, α RS)-fenvalerate in various kinds of aqueous suspension under sunlight or dark conditions.

week irradiation, while less than 5% of the applied ^{14}C was evolved as H^{14}CN . Under dark conditions, fenvalerate was fairly stable in either distilled water or 2% aqueous acetone, since more or less 80% of fenvalerate remained in each suspension after 6 weeks. Fenvalerate was gradually decomposed in both river and sea water without sunlight, with concomitant increase of H^{14}CN rather than $^{14}\text{CO}_2$. These findings suggested that H^{14}CN derived from degradation of fenvalerate was decomposed further to $^{14}\text{CO}_2$ by sunlight in water. The degradation of fenvalerate in slight alkaline river and sea water may be largely attributed to alkaline hydrolysis, because temperature of each water rose up to 50°C outdoors even in the dark. No significant change was observed in pH and dissolved oxygen (8–9 ppm) of each aqueous suspension throughout the experiment.

Table 3 shows the amounts of fenvalerate and its degradation products after ^{14}CN -, ^{14}CO - and $^{14}\alpha$ -fenvalerate in distilled water were exposed to sunlight or held in the dark. The photodegradation half-life of ^{14}CO - and $^{14}\alpha$ -fenvalerate estimated during January and February was about 14 days, and so considerably larger than that of ^{14}CN -fenvalerate measured in summer.

As major photodegradation products, decarboxy-fenvalerate, Cl-Vacid, PBacid as well

as $^{14}\text{CO}_2$ were identified. The amounts of decarboxy-fenvalerate rapidly increased, accounting for 19% of the applied ^{14}C one week after exposure to sunlight in summer, but decreased afterwards, suggesting that this product was degraded further to more polar compounds. However, in water, the amounts of decarboxy-fenvalerate was approximately 20% of the radiocarbon after 6-week exposure. The other products derived by cleavage of ester linkage of fenvalerate such as Cl-Vacid and PBacid also increased with time in winter, accounting for 57.5% and 42.6% of the applied ^{14}C six weeks after irradiation, respectively. In addition, CONH_2 -fenvalerate, COOH -fenvalerate, PBCN, CONH_2 -PPA, PBalc and PBald were detected in winter to a minor extent. These products were also found in almost the same proportion in 2% aqueous acetone, river and sea water.

Under the dark conditions, these products were formed in much less amounts than those under sunlight, indicating that these products were mainly derived from photochemical reaction of fenvalerate in water.

Degradation rate of ^{14}C -fenvalerate on three types of soil was compared between under irradiated and under dark conditions, as shown in Fig. 2. Although sunlight significantly accelerated the degradation of fenvalerate, the rate of photodegradation was different,

Table 3 Relative amounts of fenvalerate and its degradation products volatilized from, and remaining in, aqueous suspension of $^{14}\text{CN}^-$, $^{14}\text{CO}^-$ and $^{14}\text{C}\alpha$ -fenvalerate in distilled water under sunlight or dark conditions.

	% of applied ¹⁴ C											
	¹⁴ CN-Fen				¹⁴ CO-Fen				¹⁴ Cα-Fen			
	Sunlight		Dark		Sunlight		Dark		Sunlight		Dark	
	Exposure periods (Weeks)								Sunlight		Dark	
	1	4	1	4	2	6	2	6	2	6	2	6
Volatile ¹⁴ C	24.9	65.2	6.9	10.5	10.7	18.7	1.7	2.2	2.1	4.5	0.3	0.6
Polyurethane trap	0.2	1.0	0.1	0.1	0.6	0.6	0.8	0.8	0.7	0.9	0.3	0.6
NaOH solution	24.7	64.2	6.8	10.4	10.1	18.1	0.9	1.4	1.4	3.6	<0.1	<0.1
CO ₂	22.6	58.4	2.0	2.9	10.1	18.1	0.9	1.4	0.9	2.9	<0.1	<0.1
HCN	1.6	5.3	2.7	4.9	—	—	—	—	—	—	—	—
Others	0.5	0.5	2.1	2.6	<0.1	<0.1	<0.1	<0.1	0.1	0.1	<0.1	<0.1
Aqueous ¹⁴ C	69.2	27.9	92.2	88.3	86.4	71.3	96.4	93.2	98.2	93.8	101.6	100.6
Fenvalerate	33.5	0.4	89.6	85.3	49.0	11.6	95.6	87.0	53.9	16.8	90.9	89.2
Decarboxy-Fen	19.0	7.2	0.7	1.8	—	—	—	—	9.6	19.6	1.1	0.8
CONH ₂ -Fen	1.2	1.5	0.5	0.6	1.0	0.5	<0.1	<0.1	1.9	3.7	0.5	0.4
COOH-Fen	0.4	<0.1	<0.1	<0.1	0.3	0.3	<0.1	<0.1	<0.1	1.0	<0.1	0.2
PBCN	1.8	1.5	<0.1	<0.1	—	—	—	—	1.3	2.0	0.3	0.2
CONH ₂ -PPA	<0.1	2.2	<0.1	<0.1	—	—	—	—	<0.1	<0.1	<0.1	<0.1
PPA	<0.1	3.3	<0.1	<0.1	—	—	—	—	0.9	1.3	<0.1	<0.1
Cl-Vacid	—	—	—	—	34.8	57.7	<0.1	6.2	—	—	—	—
PBald	—	—	—	—	—	—	—	—	2.4	0.7	0.6	0.5
PBalc	—	—	—	—	—	—	—	—	0.5	0.7	<0.1	<0.1
PBacid	—	—	—	—	—	—	—	—	23.3	42.6	5.1	6.7
Others	13.3	11.8	1.4	0.6	1.3	1.4	0.8	<0.1	4.3	5.4	3.1	2.6
Total ¹⁴ C	94.1	93.1	99.1	98.8	97.1	90.0	98.1	95.4	100.3	98.3	101.9	101.2

Fig. 2 Degradation of ^{14}C -[2S, α RS]-fenvalerate on soil surface under sunlight or dark conditions.

Table 4 Relative amounts of ^{14}C -[2S, α RS]-fenvalerate and its degradation products on soil surface under sunlight or dark conditions.

	% of Applied ¹⁴ C											
	Kodaira soil				Katano soil				Azuchi soil			
	Sunlight		Dark		Sunlight		Dark		Sunlight		Dark	
	Exposure periods (Days)											
	3	10	3	10	3	10	3	10	3	10	3	10
Extract ¹⁴ C												
Fenvalerate	22.2	12.3	86.0	63.6	67.2	48.0	90.8	85.9	60.4	36.6	88.2	69.3
Decarboxy-Fen	0.2	0.6	0.8	1.4	0.5	1.0	0.7	1.2	0.5	1.1	0.6	1.3
CONH ₂ -Fen	28.4	25.7	3.1	17.5	4.5	7.9	0.8	3.3	13.9	22.4	2.6	9.9
CONH ₂ -Desphenyl-Fen	1.0	0.6	<0.1	<0.1	0.5	0.6	<0.1	<0.1	0.6	0.7	<0.1	<0.1
COOH-Fen	1.2	1.3	0.7	0.7	1.4	1.8	0.2	0.5	1.3	1.6	0.3	0.6
PBalc	0.4	0.4	0.4	0.2	0.9	0.7	0.5	0.4	0.7	0.6	0.4	0.3
PBacid	0.4	2.5	1.0	0.1	2.1	1.3	3.5	3.8	1.2	1.2	3.6	3.6
Others	1.0	2.8	0.2	0.1	8.4	9.7	0.4	0.2	6.2	7.5	0.4	0.3
Subtotal	54.8	46.2	92.2	85.5	85.5	71.0	96.9	95.3	84.8	71.7	96.1	85.3
Bound ¹⁴ C	39.1	47.5	3.3	6.9	8.1	12.8	1.6	2.4	6.0	9.5	1.6	2.7
Total ¹⁴ C	93.9	93.7	95.5	92.4	93.6	83.8	98.5	97.7	90.8	81.2	97.7	88.0

depending on the soil used, with a half-lives of approximately 2, 6 and 18 days in Kodaira, Azuchi and Katano soil, respectively. Under dark conditions, recovery of fenvalerate from Kodaira, Azuchi and Katano soil was approximately 55, 70 and 83% of the applied ^{14}C after 20 days, respectively. Relatively little amounts of the radiocarbon volatilized from soil surface under either irradiated or dark conditions, since more than 90% of the applied ^{14}C remained in each soil *tlc* plates during the experiments. With concomitant decrease of fenvalerate, the amounts of bound ^{14}C increased, accounting for approximately 60% after 20 days in Kodaira soil with higher organic matter content, whereas less than 10% of the applied ^{14}C was bound to Azuchi and Katano soil with lower organic matter content. The amounts of bound ^{14}C under dark conditions were much less than those under sunlight, suggesting that the bound ^{14}C was derived at least in part from photodegradation products.

Table 4 shows the relative amounts of the degradation products 3 and 10 days after application of $^{14}\text{C}\alpha$ -fenvalerate to each soil under sunlight or dark conditions. In any soils tested, CONH_2 -fenvalerate was a major degradation product, accounting for 25.7, 7.9 and 22.4% of the applied ^{14}C after 10 days in Kodaira, Katano and Azuchi soil, respectively. Although CONH_2 -fenvalerate was also detected under dark conditions, rate of formation of this product was much less than under sunlight irradiation, indicating that sunlight accelerated transformation of fenvalerate to CONH_2 -fenvalerate on soil surface. The other products such as COOH -fenvalerate, CONH_2 -desphenylfenvalerate, PBalc and PBacid were also detected, but in lesser amounts.

Four replicate measurements determined the quantum yield of fenvalerate to be 6.8×10^{-3} within all experimental error. According to Eq. 6, the half-life of disappearance of fenvalerate at shallow depth at 40 degree North Latitude was calculated to be 4.1 days and 12.4 days in summer and in winter, respectively. The calculated half-lives were nearly the same as those observed in outdoor experiments. In the same way, the half-lives of fenvalerate were calculated as a function of season and

Fig. 3 Dependence of half-life of fenvalerate upon season and northern latitude.

latitude and the results are shown in Fig. 3. The results indicate that half-lives at higher than 40 degree northern latitude increase significantly with increasing latitude from fall to winter, whereas no significant difference is observed in spring and in summer. At less than 20°N, the half-lives are almost same all the year round.

Depth dependence of the direct photolysis of fenvalerate in distilled water at 40 degree North Latitude was calculated according to Eq. 5, using attenuation coefficient of pure water.¹⁶⁾ The results are expressed as relative photolysis rates, as shown in Fig. 5. The photolysis rate of fenvalerate was approximately one half and one tenth at 50 and 300 cm in depth of that near the water surface, respectively, and decreased more rapidly in winter than in summer.

DISCUSSION

In the environment, chemicals are transformed by a number of different photochemical processes. One of these processes is a direct photolysis which involves direct absorption of sunlight followed by chemical reaction. Other processes are indirect or sensitized photolysis, which is initiated via absorption of sunlight by other chemicals. Recent studies have shown that naturally occurring substances such as humic acid, tryptophan and tyrosine act as a photosensitizer towards some kinds of pesticides in the environment.¹⁷⁻²²⁾ The photosensitizer not only accelerates the photolysis rates, but sometimes alters the photodegradation path-

Table 5 Half-life values for fenvalerate under sunlight or dark conditions.

	Half-life (Days)		
	Summer	Fall	Winter
Water			
Distilled water	4.0 (>42)		13.7 (>42)
2% Aqueous acetone	3.9 (>42)		16.0 (>42)
River water	3.5 (10)		15.0 (>42)
Sea water	3.6 (6)		14.5 (>42)
Soil			
Kodaira		1.8 (>20)	
Katano		18.0 (>20)	
Azuchi		5.8 (>20)	

ways significantly.^{19,23,24)} In the experiments presented here, photodegradation of fenvalerate was hardly sensitized in natural water, indicating that photochemical transformation proceeded mainly by direct photolysis, although the UV spectrum of river water showed the almost the same as that of humic acid and sea water exhibited the maximum absorption at 290 nm.

The natural water was filter-sterilized to preclude the microbial degradation of fenvalerate during the photolysis experiments. Immediately after filter-sterilization, microbials were hardly detected on the nutrient agar, but the number of the colonies increased to approximately 10^2 /ml after 6 weeks. However, these populations were much less than those in natural water (10^5 /ml). In consist with the above findings, the degradation half-life of fenvalerate was more than 6 weeks in the sterilized water and approximately 2 weeks in natural water,²⁵⁾ indicating that degradation of fenvalerate in sea and river water under sunlight irradiation was mainly attributed to photochemical reactions.

Table 5 summarizes the half-lives of photolysis of fenvalerate under various conditions. Although fenvalerate was rapidly photo-decomposed in water and on soil by natural sunlight, these kinetic data can not be extrapolated to other locations, because the intensity of solar ultraviolet radiation changes as a function of season and latitude.¹⁵⁾ Zepp *et al.* developed the methods to compute the half-lives for direct photolysis of various pesticides in an aquatic environment as a function of season and latitude and found the calculated half-lives to be in accord with the experimental

values within $\pm 30\%$ error.^{7,13,21,22,26,27)} The calculated half-life value of fenvalerate in distilled water at 40 degree North Latitude was also close to that of outdoor experiments. Accordingly, it is possible to estimate the photolysis half-life of fenvalerate in any season and at any latitude, as shown in Fig. 3. As was the case of other pesticides, the latitudinal variation of photolysis rate of fenvalerate is relatively small during summer, but prominent from fall to winter, especially at higher latitude, due to significant decrease of sunlight intensity in the ultraviolet region as compared with that in visible region.

Photolysis rates are also dependent on the depth of water layer and height from the sea level.¹⁵⁾ As the sunlight penetrates into a water layer, its intensity decreases, and spectral distribution changes markedly, due to attenuation derived from light absorption

Fig. 4 Calculated depth dependence of direct photolysis rate of fenvalerate at 40 degree north latitude.

Fig. 5 Photodegradation pathways for fenvalerate.

and scattering. In distilled water, photolysis rates of fenvalerate at 50 cm in depth was approximately one half of that near the water surface. As the underwater pathlength of direct sunlight increases, the depth dependence becomes more pronounced, i.e. with increasing northern latitude and from summer to winter, as shown in Fig. 4. In this case, attenuation due to scattering was ignored, since attenuation due to scattering was less important than attenuation by absorption, especially in the ultraviolet region, as was the case of most natural water.^{28,29} However, scattering seems to have more pronounced effects on the depth dependence in turbid lakes and rivers.³⁰

Based upon the identified products, the proposed degradation pathways for fenvalerate are shown in Fig. 5. Decarboxylation and cleavage of acylcarbon-oxygen bond yielding PBacid and Cl-Vacid were predominant in water, with decarboxy-fenvalerate, PBacid and Cl-Vacid accounting for approximately 20, 43 and 58% of the applied ¹⁴C, respectively. Especially in summer, the decarboxy-fenvalerate was degraded further to more polar products including 3-phenoxybenzoic acid and 3-hydroxybenzoic acid.²⁵

Recently, Holmsted *et al.* showed that the yield of decarboxy-fenvalerate exceeded 70% of the total reaction mixture when fenvalerate was irradiated with UV light (>290 nm) in water-acetonitrile (40:60), whereas PBacid and Cl-Vacid accounted for 1.5 and 6%, respectively, under the same conditions.⁶ These quantitative differences may be mainly

attributed to energy distribution and intensity between sunlight and UV light and/or to solvent (acetonitrile).

In contrast, on soil surface, a major photodegradation pathway was hydration of CN to CONH₂ yielding CONH₂-fenvalerate and was different from photolysis on glass plates or cotton leaves, with decarboxylation being dominant in the latter cases.⁶ Thus, degradation pathways also changes significantly, depending on the reaction medium.

Although fenvalerate was extensively photodecomposed, these photoproducts are not likely either to persist or to be hazardous in the environment, since CONH₂-fenvalerate, a major photoproduct on soil, as well as minor products such as COOH-fenvalerate, CONH₂-desphenylfenvalerate, PBalc and PBacid was found to be intermediates of degradation to CO₂ in soils,⁹ and decarboxy-fenvalerate, PBacid and Cl-Vacid, major photoproducts in water, were less toxic than fenvalerate to killifish, with TLM₄₈ values of more than 10 ppm.²⁵ In addition, fenvalerate and its degradation products did not tend to accumulate to high degree in fish, snail, daphnia and algae in aquatic model ecosystem.⁴

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要 約

フェンバレレート (スミサイジン®) の水中および土壌表面上における光分解

三上信可, 高橋尚裕, 林久美子, 宮本純之
蒸留水, 2% アセトン水, 河川および海水水中のフェンバレレートに太陽光線を照射すると, フェンバレレートはいずれの水中においても速やかに分解され, また, 水の種類によりその光分解速度に著しい差は認められなかった. 光分解半減期は夏季で約 4 日, 冬季で約 13~15 日であった. フェンバレレートの蒸留水中における量子収量は 6.8×10^{-8} であり, この値と specific rates of sunlight absorption 値から計算により求めた北緯 40° における半減期は夏季で 4.1 日, 冬季で 12.4 日と実測値とほぼ一致した. 土壌表面上においても, フェンバレレートの分解は太陽光線により促進されるが, その分解速度は土壌により異なり半減期は小片軽植土で 2 日, 安土砂質植壤土で 6 日, 交野砂壤土で 18 日であった. フェンバレレートは太陽光線照射下でおもに酸化, 脱炭酸, エステルおよびジフェニールエーテル結合の開裂, CN 基から CONH₂ 基への水和反応, CONH₂ 基から COOH 基への加水分解により分解され, また水中において生成した HCN は速やかに CO₂ にまで分解された.