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Soil Metabolism of a New Herbicide, [^{14}C]Pyribenzoxim, under Flooded Conditions

HEE-RA CHANG,† SUK-JIN KOO,‡ KYUN KIM,† HEE-MYONG RO,§ JOON-KWAN MOON,§ YONG-HWA KIM,† AND JEONG-HAN KIM*,§

Environmental Toxicology Division, Analytical Research Center, Korea Institute of Toxicology, 100 Jang-dong, Yuseong, Daejeon 305-343, South Korea; Agrochemical Research Center, LG Chem Investment, Daejeon 305-380, South Korea; and School of Agricultural Biotechnology, Seoul National University, Seoul 151-952, South Korea

To elucidate the fate of a new pyrimidinyloxybenzoic herbicide, pyribenzoxim, a soil metabolism study was carried out with [^{14}C]pyribenzoxim applied to a sandy loam soil under flooded conditions. The material balance of applied radioactivity ranged from 96.4 to 104.4% and from 96.1 to 101.9% for nonsterile and sterile soils, respectively. The half-life of [^{14}C]pyribenzoxim was calculated to be approximately 1.3 and 9.4 days for nonsterile and sterile soils, respectively. The metabolites identified during the study were 2,6-bis(4,6-dimethoxypyrimidin-2-yloxy)benzoic acid (**M1**) and 2-hydroxy-6-(4,6-dimethoxypyrimidin-2-yloxy)benzoic acid (**M2**), resulting from the cleavage of the ester bond and subsequent hydrolysis. The nonextractable radioactivity levels increased to 37.8% for nonsterile conditions at 50 days after treatment and to 38.2% for sterile conditions at 60 days after treatment. Fractionation of the nonextractable soil residues indicated that bound radioactivity was associated mainly with humin fraction. No significant volatile products or [^{14}C]carbon dioxide was observed during the study. On the basis of these results, pyribenzoxim is considered to undergo rapid degradation in soil by microbial and chemical reactions, mainly hydrolysis, which limits its transfer to and accumulation in lower soil layers and groundwater. Therefore, the possibility of environmental contamination from the use of pyribenzoxim is expected to be very low.

KEYWORDS: Pyribenzoxim; herbicide; soil metabolism; flooded

INTRODUCTION

Pyribenzoxim [benzophenone O-[2,6-bis(4,6-dimethoxypyrimidin-2-yloxy)benzoyl]oxime] (*1*, *2*), a new pyrimidynyloxybenzoic herbicide analogous to pyrithiobac (*3*−*6*), bispyribac-sodium (*7*−*9*), pyriminobac-methyl (*10*, *11*), and pyriftalid (*12*), was developed by LG Chemical Ltd., Korea, for postemergence treatment in rice fields. Similar to sulfonylurea herbicides, this compound was known as an inhibitor of acetolactate synthase (ALS) involved in the biosynthesis of the branched-chain amino acids in plants (*13*, *14*) and showed a maximal level of inhibition in whole plants within 24 h after treatment (*15*). No phytotoxicity was observed, and low acute toxicity (rat, oral) of >5000 mg/kg was reported (*1*, *16*). The LC_{50} for common carp (*Cyprinus carpio* L.) in 96 h was >10 mg/L. The Log *P* measured by using the shake flask method is 3.04, whereas the solubility (25 °C) in water is 3.5 mg/L and the vapor pressure (25 °C) is $<7.4 \times 10^{-5}$ mmHg (*16*, *17*). The BCF value was 33.2 for common carp (*C. carpio*), suggesting that the possibility of biocentration was very low in the aquatic environment (*18*). However, only limited information has been available on the environmental fate and metabolism of pyribenzoxim.

A certain fraction of applied pesticide reaches the soil through various types of mechanisms. Even when applied to crops, some may reach the soil directly through spray drift or fumigation and indirectly through wash-off. A variety of transformed products can subsequently be formed through biotic or abiotic reactions. Pesticide movement and distribution in soils have received increased attention during recent years because of concern over potential effects on surface water and groundwater quality. Soil metabolism studies of pesticides are very important for predicting the degradation behavior of the parent pesticide and determining the nature and extent of the metabolites, as well as for assessing the potential environmental hazards.

In the present investigation, an experiment was conducted to study the biotic and abiotic degradation behavior of [^{14}C]-pyribenzoxim and to identify major metabolites in soil under flooded conditions.

MATERIALS AND METHODS

Chemicals. The radiolabeled test compounds [*carbonyl*-^{14}C]pyribenzoxim (**P1**) and [*ring*-^{14}C(U)]pyribenzoxim (**P2**), non-radiolabeled pyribenzoxim, and its metabolites, 2,6-bis(4,6-dimethoxypyrimidin-2-

* Corresponding author (telephone +82-2-880-4644; fax +82-2-873-4415; e-mail kjh2404@snu.ac.kr).
† Korea Institute of Toxicology.
‡ LG Chem Investment.
§ Seoul National University.

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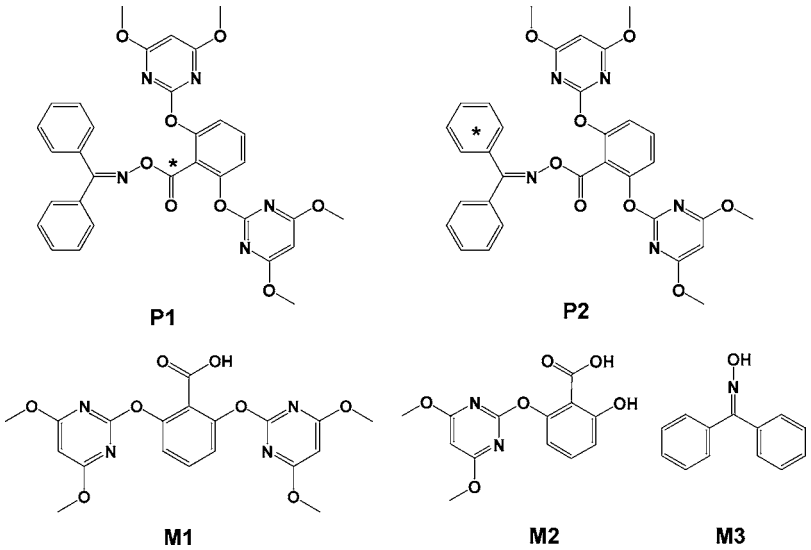

Figure 1. Structures of [*carbonyl*-^{14}C]LGC-40863 (**P1**), [*ring*-^{14}C(U)]LGC-40863 (**P2**), and metabolites (**M1**, **M2**, and **M3**). The site of the ^{14}C label is marked with an asterisk.

Table 1. Physicochemical Properties of the Test Soil

pH[a]	organic carbon[b] (%)	CEC (mequiv/100 g)	sand[c] (%)	silt[c] (%)	clay[c] (%)	texture (USDA)
7.3	1.6	8.6	66.7	24.9	8.3	sandy loam

[a] Measured in 1:5 soil/deionized water suspension (*19*). [b] Walkley–Black colorimetric determination (*20*). [c] Particle-size analysis: hydrometer method (*21*).

yloxy)benzoic acid (**M1**), 2-hydroxy-6-(4,6-dimethoxypyrimidin-2-yloxy)benzoic acid (**M2**), and benzophenone oxime (**M3**), were kindly provided by LG Chem Investment (**Figure 1**). The radiochemical purities were >98%, and specific activities of **P1** and **P2** were 3.37 and 3.40 MBq/mg, respectively. Both compounds were used without further purification. HPLC grade acetone, dichloromethane, acetonitrile, and methanol were purchased from Burdick and Jackson. All of the other reagents and common chemicals were of analytical grade.

Test Soil. Sandy loam soil was collected from the top 20 cm of a drained paddy field in Daejeon, Korea. After air-drying at room temperature for 24 h, soil was passed through a 2 mm sieve to remove small stones, fauna, and plant debris prior to being characterized (**Table 1**; *19*−*21*). The soil was stored at −20 °C to maintain microbial activity prior to use. Sterile soil was prepared by autoclaving at 15 psi and 120 °C for 20 min (*22*).

Radioassay. Radioactivity of all liquid samples was measured by liquid scintillation counting (LSC), using a model LS 6000TA (Beckman) liquid scintillation counter with external quench correction. Ultima Gold XR (5 mL) was used for the aqueous samples, Hionic fluor (5 mL) was used for CO_2 trapping agent (0.5 N NaOH solution), and Insta-fluor (10 mL) was used for organic samples. The nonextractable soil residue (200 mg) was combusted by an oxidizer (Packard model 307) after mixing with Combustaid (100−200 μL). The [^{14}C]-carbon dioxide produced was absorbed in Carbo-sorb E (5 mL) and mixed with Permafluor E^{++} scintillation cocktail (10 mL) for LSC counting.

Chromatography. Determination of radioactivity and identification of pyribenzoxim and metabolites were performed on a Thermo Separation Product model P2000 HPLC system equipped with UV−vis detector and radioactivity monitor (Packard Radiomatic 150TR, 500 μL/min liquid cell) by cochromatography with authentic compounds. A reverse phase Luna C_{18} column (4.6 × 250 mm, 5 μm, Phenomenex) was used. The column was eluted with a mobile phase (80% acetonitrile in water containing 0.1% trifluoroacetic acid) for 20 min at the flow rate of 1.0 mL/min. UV detection (247 nm) was performed with a variable-wavelength detector. Radioactivity monitoring was performed using scintillation cocktail (Ultima Flo-M, 2 mL/min). Under these conditions, the retention times of pyribenzoxim, **M1**, **M2**, and **M3** were approximately 10.5, 6.7, 4.8, and 7.4 min, respectively.

Extraction Efficiency. After soil samples (80 g, air-dry weight) were weighed into a incubation flask (100 mL), 65 mL of distilled water was added to achieve flooded conditions with a water layer of 2.5 cm per OECD guidelines and then [^{14}C]**P1** (14.07 kBq), **M1**, **M2**, and **M3** in methanol (10 mg/L solution) were treated at a concentration of 0.05 mg/kg. Following treatment, the soil was thoroughly mixed. After 30 min, samples of treated soil were extracted sequentially with 100, 50, and 50 mL of acetone, followed by a second phase extraction with acetone/water/36% HCl (35:35:2, v/v, 50 mL). Each extraction was performed by shaking for 1 h. Each extract was centrifuged at 3000 rpm for 10 min, and the supernatant was pooled. Triplicate aliquots (1 mL) of soil extracts were analyzed by LSC to measure the radioactivity.

Soil Incubation. The soil (80 g, air-dry weight) was weighed into the incubation flask (150 mL) and flooded with 65 mL of sterilized distilled water. The soil samples were incubated in a flow-through system at 20 ± 2 °C for 2 weeks in the dark prior to treatment. Air was passed through the system at a flow rate of 10 mL/min via a sodium hydroxide aqueous solution (0.1 M) to remove carbon dioxide followed by distilled water to humidify. Soil incubation under sterilized conditions was conducted in the same manner except the use of sterilized soil in a clean bench. After preincubation, **P1** (5.42 kBq) and **P2** (5.42 kBq) in methanol (540 μL of a 3 mg/L solution) were applied to the soil at a rate of 0.04 mg/kg (dry weight basis), equivalent to an approximate field use rate of 0.05 kg/ha (*23*). Treated soil samples were then again incubated in a flow-through system at 20 ± 2 °C for 50 days (nonsterile soil samples) or 60 days (sterile soil samples) in the dark. Two XAD-2 traps and two sodium hydroxide solution traps (0.5 M, 40 mL) in sequence were used to collect volatile compounds and [^{14}C]carbon dioxide, respectively, which potentially evolved from the soil. Microbial population was measured at each sampling date with nonsterile soil samples. For control experiments, untreated soil samples and soil samples containing the same amount of solvent for pyribenzoxim treatment were incubated under the same conditions. The treated soil was sampled at 0, 3, 6, 12 h, 1, 3, 7, 21, and 50 days after treatment (DAT) for nonsterilized conditions and at 0, 1, 3, 7, 14, 30, and 60 DAT for sterilized conditions. At all sampling dates, the redox potential, dissolved oxygen (DO), and pH were measured. The redox potential and pH were measured by pH/mV/ORP meter (model 720A, Orion) equipped with a model 97-78 ORP probe and a model 91-57 pH electrode. DO was measured by an oxygen meter (Multi 3401, WTW) equipped with a model cell ox 325 oxygen sensor. Triplicate aliquots (1 mL) of methanol extract of XAD-2 and sodium hydroxide solution from traps were counted at the sampling date by LSC for total radioactivity.

Extraction and Analysis of Soil. At all soil sampling dates, three flasks per treatment were taken and each soil sample was extracted sequentially with 100, 50, and 50 mL of acetone, followed by acetone/water/36% HCl (35:35:2, v/v, 50 mL) by shaking for 1 h. Each extract was centrifuged at 3000 rpm for 10 min, and then the supernatant was taken and pooled. The pooled extract was concentrated to about 50 mL by a rotary evaporator. Saturated sodium chloride solution (50 mL) was added to the residual aqueous phase, and the mixture was acidified to pH 2 with sulfuric acid (10 N; 1 mL), which was then extracted three times with 100, 50, and 50 mL of dichloromethane. The dichloromethane extracts were passed through anhydrous sodium sulfate and evaporated to remove organic solvent. The residue was dissolved in methanol (1 mL), and the aliquot was analyzed by LSC and RHPLC to determine the concentrations of parent compound and its metabolites. All of the postextracted soil samples were air-dried and pulverized before triplicate portions (each 200 mg) of them were combusted with an oxidizer for LSC counting.

Distribution of Solvent Nonextractable Radioactivity in Soil. Nonextractable soil-bound residues were fractionated with strong base and acid into three fractions of humin, humic acid, and fulvic acid (*24*, *25*). Postextracted soil samples (2 g, dry weight equivalents) were extracted with sodium hydroxide solution (0.1 M, 5 mL). The extract was centrifuged at 3000 rpm for 10 min, and the supernatant (fulvic and humic fraction) was decanted. This procedure was repeated until the radioactivity of the extract reached background level, and the extracts were combined. Hydrochloric acid (11.3 M, 1 mL) was added to the combined extract to adjust the pH to 1. The mixture was extracted and centrifuged, and the supernatant (fulvic acid fraction) was decanted. The resulting precipitate (humic acid fraction) was washed with hydrochloric acid (0.2 M, 5 mL) with centrifugation and was combined with the fulvic acid fraction for LSC counting. The humic acid precipitate was redissolved in sodium hydroxide (0.1 M, 5 mL) before radiocounting (1.0 mL). Triplicate subsamples (250 mg) of the residue (humin fraction) were combusted to determine the content of radioactivity.

Assay for Microorganism Population. Triplicate portions (each 1 g) were taken from soil samples for microbial assay at the each sampling dates. The soil was suspended in 9 mL of sterilized distilled water. An aliquot (100 μL) of the suspension was taken and diluted 10^4-10^5-fold. Triplicates of aliquots (each 100 μL) were taken from the serial dilutions and placed on agar plates. For microorganism population counting, the nutrient broth agar was prepared by dissolving 8 g of nutrient broth agar and 15 g of bacto agar in 1 L of distilled water, and the plates were incubated at 30 °C for 3 days (*26*, *27*). The total number of colonies was recorded using the dilution plate method.

The dry weight of soil was determined so that the number of microorganisms per gram of soil could be calculated.

Calculation of Half-Life. Pseudo-first-order kinetics was assumed for calculation of half-life values. Data were subjected to a linear regression analysis (ln of mean % residual pyribenzoxim versus time) using SigmaPlot 4.0 software (SPSS Science).

RESULTS AND DISCUSSION

Extraction Efficiency. [^{14}C]Pyribenzoxim, **M1**, **M2**, and **M3** were recovered from soil with high yield and reproducibility of 96.7 ± 5.2, 86.5 ± 6.7, 96.3 ± 3.0, and 89.3 ± 3.0%, respectively.

Test Conditions and Microorganism Population. After flooding, the redox potential (**Figure 2A**) in nonsterile soil was decreased to negative values, from −36 to −62 mV, and dissolved oxygen (**Figure 2C**) was also decreased to 0.8 mg/L. However, in sterile conditions, the redox potential was maintained at approximately 100 mV and the dissolved oxygen was >3.5 mg/L. On the basis of the classification of reduced condition by redox potential, the test conditions of sterile and nonsterile soils belong to the moderately to strictly reduced condition (*28*). The ranges of pH in nonsterile and sterile conditions were near neutral values; 6.6−8.6 and 6.7−8.1, respectively (**Figure 2B**). A negative redox potential and neutral pH are known to attain the flooded conditions within a few days after flooding (*29*−*31*). The results of microbial plate counts, including untreated and solvent-treated soil samples (*23*), indicated that the soil microorganisms remained viable throughout the study in nonsterile conditions (**Figure 3**).

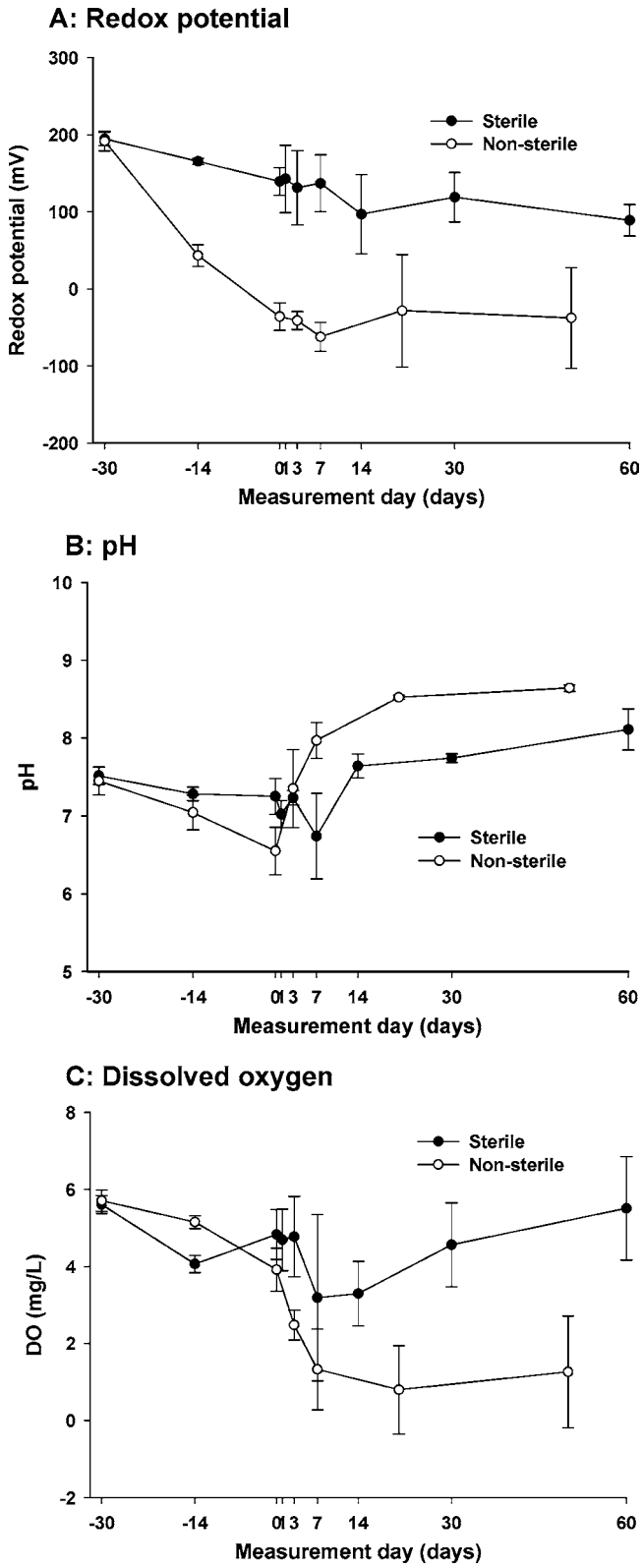

Figure 2. Changes of the redox potential (**A**), pH (**B**), and dissolved oxygen (**C**) in nonsterile and sterile soils. Days in negative scale are for preincubation period before treatment.

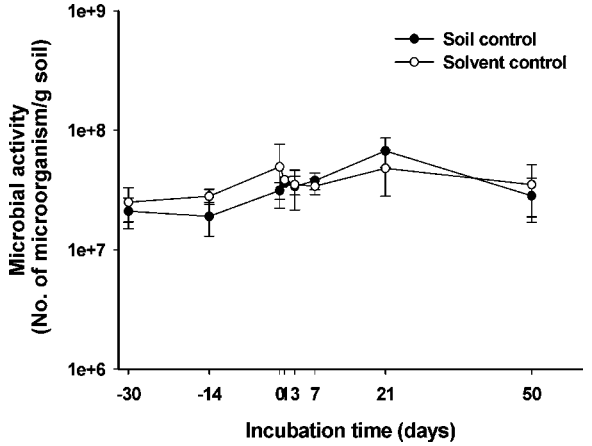

Figure 3. Change of microbial activity for soil control and solvent control in nonsterile soil. Days in negative scale are for preincubation period before treatment.

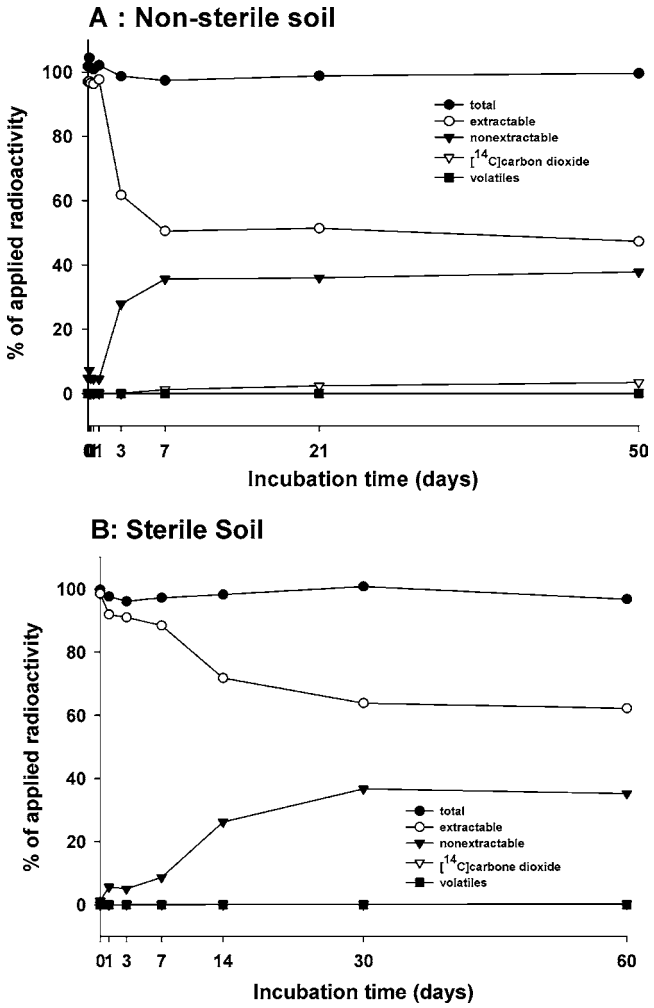

Figure 4. Distribution of radioactivity in nonsterile (**A**) and sterile soil (**B**) treated with [^{14}C]pyribenzoxim.

Material Balance. Material balance was determined by the ^{14}C activity recovered in extracts, $^{14}CO_2$, volatile compounds, and bound residues. The average material balances of nonsterile and sterile soil were 96.4−104.4% (**Figure 4A**) and 96.1−101.9% (**Figure 4B**) of applied radioactivity, respectively. The radioactivity of the solvent extract from nonsterile soil decreased

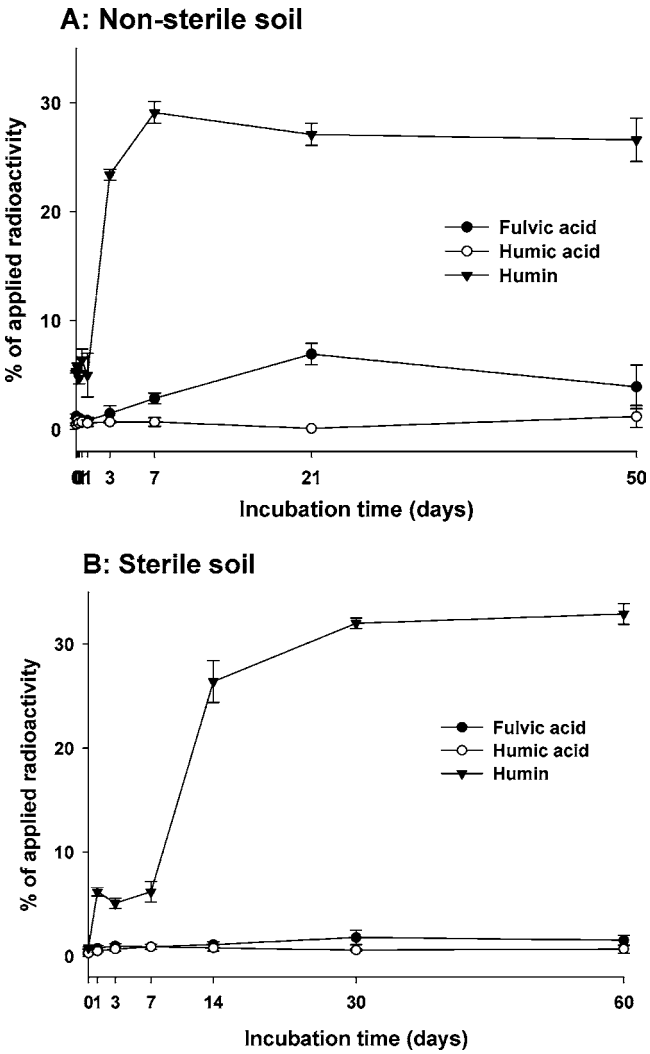

Figure 5. Distribution of solvent-nonextractable radioactivity in nonsterile (**A**) and sterile soil (**B**) treated with [^{14}C]pyribenzoxim.

rapidly until 7 DAT (**Figure 4A**); however, that in sterile soil decreased gradually throughout the incubation time (**Figure 4B**). At the end of the study, the radioactivity of solvent extract in nonsterile and sterile soil accounted for 55.3 and 59.3%, respectively. The nonextractable radioactivity levels increased to 37.8% for nonsterile (**Figure 4A**) and to 38.2% for sterile conditions (**Figure 4B**), suggesting the binding of pyribenzoxim or its degradation products to soil. The amounts of [^{14}C]carbon dioxide evolved in nonsterile and sterile conditions were approximately 0.08−3.42 and 0.03−1.98% of the applied radioactivity, respectively, during the incubation time (**Figure 4**), which denotes that the mineralization of pyribenzoxim by soil microbes is minimal under flooded conditions. Trapping of volatile products is commonly recommended when the vapor pressure of the chemical under test is $>1 \times 10^{-5}$ mmHg at 20 °C (*32*). Although the vapor pressure of pyribenzoxim is $<7.4 \times 10^{-5}$ mmHg at 25 °C (*17*), XAD-2 was used in this study to trap any possible volatile metabolites. The volatile products in nonsterile and sterile soil accounted for <0.1% of applied radioactivity at all sampling intervals (**Figure 4**).

To determine the distribution of radioactivity in the nonextractable soil residue, further fractionation of the residue into humin, humic acid, and fulvic acid was performed. In nonsterile soil, 3.9, 26.6, and 1.2% of applied radioactivity were found in fulvic acid, humin, and humic acid fractions, respectively, at 50 DAT (**Figure 5**), whereas the levels in sterile soil at 60 DAT

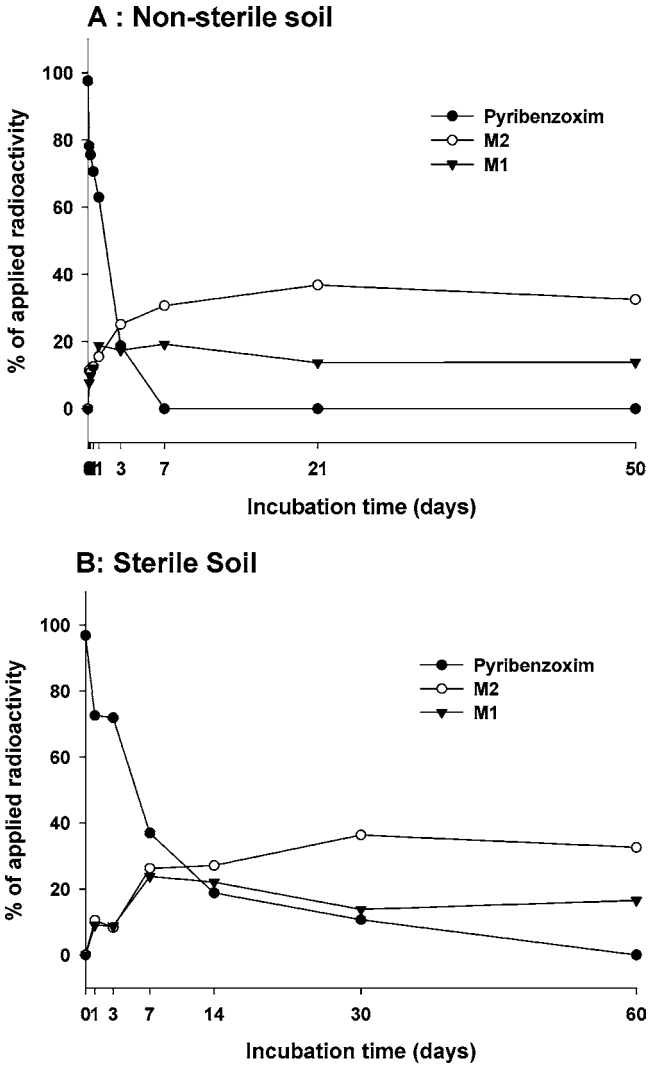

Figure 6. Degradation pattern of [^{14}C]pyribenzoxim and transformation of metabolites in nonsterile (**A**) and sterile soil (**B**) under flooded conditions.

were 1.5, 32.9, and 0.7%, respectively. The results indicated that bound radioactivity was associated mainly with the humin fraction, similar to those reported for a new herbicide, LGC-42153 (*33*), and ethaboxam (*34*).

Degradation of [^{14}C]Pyribenzoxim and Identification of Metabolites. Peaks of [^{14}C]pyribenzoxim, **M1**, and **M2** were well separated to distinguish from each other and as well as from other interfering peaks on a C_{18} column under the present elution conditions employed for this study. **M1** and **M2** were identified by comparison of their HPLC retention times with those of authentic standards for nonsterile and sterile soils. [^{14}C]-Pyribenzoxim degraded rapidly and was not detected at 7 DAT for nonsterile soil and at 60 DAT for sterile soil. The major degradation products were **M1** and **M2**. In nonsterile soil, **M1** reached maximum concentration (19.2% of applied radioactivity) at 7 DAT, whereas **M2** gave maximum concentration (36.8% of applied radioactivity) at 21 DAT (**Figure 6**). In sterile soil, the maximum concentrations of **M1** (23.8% of applied radioactivity) and **M2** (36.3% of applied radioactivity) were observed at 7 and 30 DAT, respectively (**Figure 6**). Disappearance of pyribenzoxim and formation of **M1** and **M2** were more rapid in nonsterile soil.

The estimated half-lives ($t_{1/2}$) of [^{14}C]pyribenzoxim were calculated as 1.3 and 9.4 days for nonsterile and sterile soils, respectively. These short half-lives of [^{14}C]pyribenzoxim in

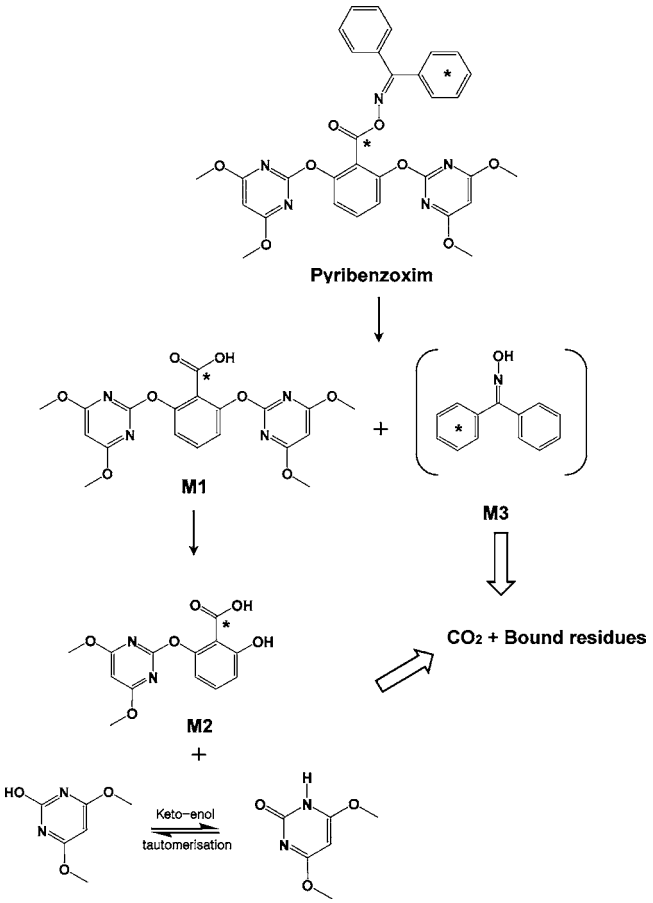

Figure 7. Proposed metabolic pathway of pyribenzoxim in soil under flooded conditions.

flooded soil were similar to those of other pyrimidinyloxybenzoic acid herbicides such as pyriftalid and bispyribac-sodium, which were degraded rapidly in flooded paddy soil with half-life values of 5−10 days (*16*, *35*). Other degradation studies of pyribenzoxim including direct and indirect aqueous photolysis also showed relatively short half-life values of 9.2−26.9 days (*36*).

On the basis of these results, the metabolic pathway of pyribenzoxim in flooded soil was proposed as shown in **Figure 7**. The degradation of pyribenzoxim was initiated by ester hydrolysis to form **M1** and **M3**, and then **M1** was further hydrolyzed to cleave the ether linkage, generating **M2** in both biotic and abiotic systems. Such ester hydrolytic reactions of pyribenzoxim were reported at 2,4-D, 2,4,5-T, and pyrethroids, whereas the cleavage of the ether bridge of the aromatic ring has been commonly found in fenvalerate, clomethoxynil, and permethrin in aerobic upland soils (*37*). The metabolites **M1**, **M2**, and **M3** were characterized by Liu et al. (*38*) as the urinal and fecal metabolites of pyribenzoxim in rats. The degradation mechanism of pyribenzoxim involving an ester hydrolysis was also proposed in previous studies (*35*, *36*). However, **M3** formed by ester hydrolysis of pyribenzoxim was not observed in either nonsterile or sterile soils in the present study. There could be two explanations. First, **M3** may be further degraded to other small metabolites that could not be detected under the analytical conditions employed for the experiment. Second, **M3** may be preferentially bound to soil to form nonextractable soil residues. Because the metabolism of pyribenzoxim largely depends on hydrolysis, although microbial presence accelerates its degradation, the metabolic profile under nonsterile and sterile soils showed similar patterns.

In conclusion, reproducible extraction efficiency for [^{14}C]-pyribenzoxim, **M1**, **M2**, and **M3** and excellent material balances from nonsterile (96.4−104.4%) and sterile soil (96.1−101.9%) experiments provided the reliability of results obtained in this study. The half-life of pyribenzoxim was calculated to be 1.3 and 9.4 days for nonsterile and sterile soils, respectively, when pyribenzoxim was treated at a concentration of 0.04 mg/kg on a sandy loam soil flooded with distilled water at 20 ± 2 °C. Although significant abiotic dissipation of pyribenzoxim was observed under sterile condition, the microbial process accelerated the degradation of the herbicide by about 7-fold (*22*, *29*, *31*, *39*, *40*). The major metabolites formed were 2,6-bis(4,6-dimethoxypyrimidin-2-yloxy)benzoic acid (**M1**) and 2-hydroxy-6-(4,6-dimethoxypyrimidin-2-yloxy)benzoic acid (**M2**). Due to rapid degradation of pyribenzoxim, its transfer to and accumulation in lower soil layers and groundwater are considered to be limited, and hence the possibility of environmental contamination is expected to be very low. A soil metabolism study of pyribenzoxim under aerobic conditions could be performed as a complimentary study to understand more about the fate of pyribenzoxim in soil.

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LITERATURE CITED

(1) Koo, S. J.; Ann, S. C.; Chae, S. H.; Kim, J. S.; Lee, J. H.; Cho, J. H. Biological activity of the new herbicide LGC-40863 {benzophenone *O*-[2,6-bis[(4,6-dimethoxy-2-pyrimidinyl)oxy]-benzoyl]oxime}. *Pestic. Sci.* **1997**, *51*, 109−114.

(2) Koo, S. J.; Kim, J. S.; Lee, J. H. Foliar retention of the herbicide pyribenzoxim (1% EC), and its effects on herbicidal activity and rice phytotoxicity. *Korean J. Weed Sci.* **1998**, *18*, 304−313.

(3) Dotray, P. A.; Keeling, J. W.; Henniger, C. G.; Abernathy, J. R. Palmer amaranth (*Amaranthus palmeri*) and devil's-claw (*Proboscidea louisianica*) control in cotton (*Gossypium hirsutum*) with pyrithiobac. *Weed Techol.* **1996**, *10*, 7−12.

(4) Harrison, M. A.; Hayes, R. M.; Mueller, T. C. Environmental affects cotton and velvetleaf response to pyrithiobac. *Weed Sci.* **1996**, *44*, 241−247.

(5) Nezu, Y.; Wada, N.; Saitoh, Y.; Takahashi, S.; Miyazawa, T. Synthesis and herbicidal activity of pyrimidinyl salicylic and thiosalicylic acids. *J. Pestic. Sci.* **1996**, *21*, 293−303.

(6) Takahashi, S.; Shigematsu, S.; Morita, A.; Nezu, M.; Claus, J. S.; Williams, C. S. KIH-2031, a new herbicide for cotton. *Proc. Brighton Crop Prot. Conf. Weeds* **1991**, *1*, 57−62.

(7) Braverman, M. P.; Jordan, D. L. Efficacy of KIH-2031 in dry- and water-seeded rice (*Oryza sativa*). *Weed Technol.* **1996**, *10*, 876−882.

(8) Fukai, Y.; Unai, T.; Ishikawa, K.; Yusa, Y.; Wasa, N.; Tezuka, M.; Okada, S. Metabolism of ALS inhibitory herbicide bispyribac-sodium [KIH-2023] in rats. *J. Pestic. Sci.* **1995**, *20*, 479−486.

(9) Yokoyama, M.; Watanabe, O.; Kawano, K.; Shigematsu, S. KIH-2031, a new selective herbicide to control barnyardgrass in rice. *Proc. Brighton Crop Prot. Conf. Weeds* **1991**, *1*, 63−68.

(10) Hanai, R.; Kawano, K.; Shigematsu, S.; Tamaru, M. KIH-6127: a new selective herbicide to control barnyardgrass in rice. *Proc. Brighton Crop Prot. Conf. Weeds* **1993**, *1*, 41−46.

(11) Shimizu, T.; Nakayama, I.; Nakano, T.; Nezu, Y.; Abe, H. Inhibition of plant acetolactate synthase by herbicides, pyrimidinylsalicylic acids. *J. Pestic. Sci.* **1994**, *19*, 59−67.

(12) Luthy, C.; Zondler, H.; Rapold, T.; Seifert, G.; Urwyler, B.; Heinis, T.; Steinrucken, H. C.; Allen, J. 7-(4,6-Dimethoxypyrimidinyl)oxythiophthalides as novel herbicides: part 1. CGA279 233: a new grass-killer for rice. *Pest Manag. Sci.* **2001**, *57*, 205−224.

(13) Bae, Y. T.; Lee, J. H.; Koo, S. J. *In vitro* acetolactate synthase inhibition of LGC-40863 in rice and barnyardgrass. *Korean J. Weed Sci.* **1997**, *17*, 66−70.

(14) Umbarger, H. E. Amino acid biosynthesis and its regulation. *Annu. Rev. Biochem.* **1978**, *47*, 503−606.

(15) Koo, S. J.; Kim, J. S.; Kang, S. H. Antagonistic interaction of propanil and pyribenzoxim on barnyardgrass control. *Pestic. Biochem. Physiol.* **2000**, *67*, 46−53.

(16) Tomlin, C. D. S. In *The Pesticide Manual*, 13th ed.; British Crop Protection Council Press: Hampshire, U.K., 2003; pp 97, 861, 866.

(17) Liu, K. H.; Moon, J. K.; Sung, H. J.; Kang, S. H.; Koo, S. J.; Lee, H. S.; Kim, J. H. *In vivo* pharmacokinetics of pyribenzoxim in rats. *Pest Manag. Sci.* **2001**, *57*, 1155−1160.

(18) Seo, J. S.; Liu, K. H.; Chung, K. H.; Shin, J. S.; Kim, J. H. Bionconcentration and depuration of pyribenzoxim in common carp (*Cyprinus carpio*). *Bull. Environ. Cotam. Toxicol.* **2002**, *68*, 617−622.

(19) Rho, J. S. Soil pH. In *Methods of Soil Chemistry Analysis*; Han, K. H., Ed.; Rural Development Administration: Suwon, Korea, 1988; pp 26−29.

(20) Nelson, D. W.; Sommers, L. E. Total carbon, organic carbon, and organic matter. In *Methods of Soil Analysis, Part 3, Chemical Methods*; Bartels, J. M., Ed.; Soil Science Society of America: Madison, WI, 1996; pp 961−1010.

(21) Gee, G. W.; Bauder, J. W. Particle-size analysis. In *Methods of Soil Analysis, Part 1, Physical and Mineralogical Methods*; Klute, A., Ed.; Soil Science Society of America: Madison, WI, 1986; pp 383−412.

(22) Rueppel, M. L.; Brightwell, B. B.; Schaefer, J.; Marvel, J. T. Metabolism and degradation of glyphosate in soil and water. *J. Agric. Food Chem.* **1977**, *25*, 517−528.

(23) OECD. OECD guidelines for the testing of chemicals, Test No. 307, Aerobic and anaerobic transformation in soil, adopted 24 April 2002.

(24) Kim, J. H.; Kang, K. K.; Park, C. K.; Kim, K.; Kang, B. H.; Lee, S. K.; Roh, J. K. Aerobic soil metabolism of flupyrazofos. *Pestic. Sci.* **1998**, *54*, 237−243.

(25) Parsons, J. W. Isolation of humic substance from soils and sediments. In *Humic Substances and Their Role in the Environment*; Frimmel, F. H., Christman, R. F., Eds.; Wiley: New York, 1988; pp 3−14

(26) Cappuccino, J. G.; Sherman, N. *Microbiology: A Laboratory Manual*; Addsion-Wesley: New York, 1983; p 81.

(27) Han, K. K. Soil, plant, soil microbiology. In *Soil Chemical Analysis Methods*; Kim, D. S., Ed.; National Institute of Agricultural Science and Technology, Rural Development Administration: Suwon, Korea, 1988; pp 261−268.

(28) Wolfe, N. L.; Mingelgrin, U.; Miller, C. C. Abiotic transformation in water, sediments, and soil. In *Pesticide in the Soil Environment: Processes, Impact, and Modeling*; Cheng, H. H., Ed.; Soil Science Society of America: Madison, WI, 1990; pp 103−124.

(29) Siddarame Gowda, T. K.; Sethunathan, N. Persistence of endrin in indian rice soils under flooded conditions. *J. Agric. Food Chem.* **1976**, *24*, 750−753.

(30) Adhya, T. K.; Wahid, P. A.; Sethunathan, N. Persistence and biodegradation of selected organophosphorus insecticides in flooded versus non-flooded soils. *Biol. Fertil. Soils* **1987**, *4* (36), 36−40.

(31) Adhya, T. K.; Sudhakar-Barik, Sethunathan, N. Stability of commercial formulation of fenitrothion, methyl parathion, and parathion in anaerobic soils. *J. Agric. Food Chem.* **1981**, *29*, 90−93.

(32) Ou, L. T.; Thomas, J. E.; Dickson, D. W. Degradation of fenamiphos in soil with a history of continuous fenamiphos applicatioins. *Soil Sci. Soc. Am.* **1994**, *58*, 1139−1147.

(33) Kim, J.; Liu, K. H.; Kang, S. H.; Kim, K.; Ku, S. J.; Kim, J. H. Aerobic soil metabolism of a new herbicide, LGC-42153. *J. Agric. Food Chem.* **2003**, *51*, 710−714.
(34) Kim, J. H.; Lee, Y. S.; Keum, Y. S.; Kim, M. K.; Kang, S. H.; Kim, D. S. Chapter 4. Metabolism of Ethaboxam in Soil. In *Environmental Fate and Effects of Pesticides*; ACS Symposium Series 853; Coats, J. R., Yamamoto, H., Eds.; American Chemical Society: Washington, DC, 2003; pp 65−78.
(35) AGROProjects-WEEDProjects. Product Profile 2−Pyriftalid; 2003; available at http://www.pjbpubs.com/cms.asp?pageid=1100.
(36) Seo, J. S. Fish bioconcentration and aqueous photolysis of a herbicide pyribenzoxim. Thesis, Seoul National University, Seoul, Republic of Korea, 2001.
(37) Okawa, H.; Nambu, K.; Inui, H.; Miyamoto, J. Metabolic fate of fenvalerate (Sumicidin) in soil and by soil microorganisms. *J. Pestic. Sci.* **1978**, *3*, 129−141.
(38) Liu, K. H.; Moon, J. K.; Kang, S. H.; Koo, S. J.; Lee, H. S.; Kim, J. H. Identification of rat urinal and fecal metabolites of a new herbicide, pyribenzoxim. *J. Agric. Food Chem.* **2005**, *53*, 6713−6717.
(39) Schooley, D. A.; Creswell, K. M.; Staiger, L. E.; Quistad, G. B. Environmental degradation of the insect growth regulator isopropyl (2*E*,4*E*)-11-methoxy-3,7,11-trimethyl-2,4-dodecadienoate (methoprene). IV. Soil metabolism. *J. Agric. Food Chem.* **1975**, *23*, 369−373.
(40) Venkateswarlu, K.; Sidedarame Gowda, T. K.; Sethunathan, N. Persistence and biodegradation of carbofuran in flooded soils. *J. Agric. Food Chem.* **1977**, *25*, 533−536.

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