JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Article

pubs.acs.org/JAFC

Enantioselective Degradation and Enantiomerization of Indoxacarb in Soil

Dali Sun,[†,§] Junxiao Pang,[§] Jing Qiu,[#] Li Li,[⊥] Chenglan Liu,*[,†] and Bining Jiao*[,§]

[†]Key Laboratory of Natural Pesticide and Chemical Biology, Ministry of Education, Laboratory of Insect Toxicology, South China Agricultural University, Guangzhou 510642, China

[§]Laboratory of Citrus Quality and Safety Risk Assessment, Ministry of Agriculture, Citrus Research Institute, Southwest University, Chongqing 400712, China

[#]Institute of Quality Standards and Testing Technology for Agro-products, Key Laboratory of Agro-product Quality and Safety, Chinese Academy of Agricultural Sciences, Beijing 100081, China

[⊥]State Key Laboratory of Integrated Management of Pest Insects and Rodents, Institute of Zoology, Chinese Academy of Sciences, Beijing 100101, China

ABSTRACT: In this study, the enantioselective degradation and enantiomerizaton of indoxacarb were investigated in two soils under nonsterilized and sterilized conditions using a chiral OD-RH column on a reversed-phase HPLC. Under nonsterilized conditions, the degradation of indoxacarb in two soils was enantioselective. In acidic soil, the half-lives of *R*-(−)- and *S*-(+)-indoxacarb were 10.43 and 14.00 days, respectively. Acidic soil was preferential to the degradation of *R*-(−)-indoxacarb. In alkaline soil, the half-lives of *R*-(−)- and *S*-(+)-indoxacarb were 12.14 and 4.88 days, respectively. *S*-(+)-Indoxacarb was preferentially degraded. Under sterilized conditions, approximately 5−10% of the initial concentration degraded after 75 days of incubation in acidic soil, whereas in alkaline soil, approximately half of the initial concentration degraded due to chemical hydrolysis under alkaline conditions. Enantiomerization was also discovered in acidic and alkaline soils. The results showed that mutual transformation existed between two enantiomers and that *S*-(+)-indoxacarb had a significantly higher inversion rate to *R*-(−)-indoxacarb than its antipode.

KEYWORDS: *enantioselective degradation, enantiomerization, enantiopure, indoxacarb*

INTRODUCTION

Indoxacarb, methyl-7-chloro-2,5-dihydro-2-(((methoxycarbonyl)(4-(trifluoromethoxy)phenyl)amino)-carbonyl)-indeno[1, 2-*e*]-[1,3,4]-oxadiazine-4*a*(3*H*)-carboxylic acid methyl ester, is an oxadiazine insecticide that is effective against a broad spectrum of insect pests.[1] It has been chosen as a replacement for synthetic organophosphate insecticides and is used on a range of crops, including fruits, vegetables, soybeans, alfalfa, and peanuts, to control insects such as *Heliothis armigera*, *Pieris rapae*, *Plutella xylostella*, *Prodenia litura*, and *Laphygma exigua* Hubner but is harmless to numerous nontarget insects.[2,3] Indoxacarb is C-chiral due to the presence of an asymmetrically substituted C atom and contains a pair of enantiomers (Figure 1). The absolute configuration of indoxacarb was confirmed with (−) rotation of the *R*-enantiomer and (+) rotation of the *S*-enantiomer.[4] The activity of this insecticide is attributed mainly to *S*-(+)-indoxacarb.

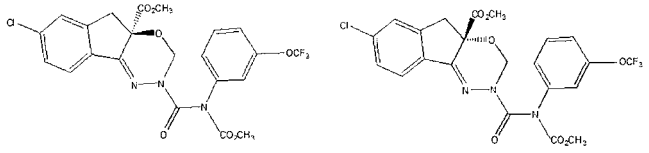

Figure 1. Chemical structures of indoxacarb enantiomers.

There are primarily three series of indoxacarb products on the market, including DPX-JW062, DPX-MP062, and DPX-KN128, which have ratios of 1:1, 1:3, and 0:1 of *R*-(−)-indoxacarb and *S*-(+)-indoxacarb, respectively.[5,6]

The enantiomer-specific profiles of chiral contaminants have become important topics at the forefront of chemistry and toxicology research. In theory, enantiomers have identical physical and chemical properties and abiotic degradation rates, whereas their individual toxicities, biological activities, and environmental fates have been shown to differ.[7−10] Microorganisms are considered as the main cause of enantioselective processes. Therefore, the enantiomeric compositions are constantly changing. In some cases, only one enantiomer is degraded while the other enantiomer is accumulated in the environment. For example, studies have shown that enantiomers of fenbuconazole, diclofop-methyl, and triadimefon behave significantly differently during biodegradation and bioaccumulation in the environment.[11−13] Additionally, enantiomerization was also found in some chiral compounds, indicating that the individual enantiomers undergo inversion of their respective configurations. Therefore, information on stereochemistry is important in assessing the environmental

Received: August 1, 2013
Accepted: October 25, 2013
Published: October 25, 2013

dx.doi.org/10.1021/jf4045952 | *J. Agric. Food Chem.* 2013, 61, 11273−11277

safety of indoxacarb, which could not be obtained from achiral analysis.

Enantioselective degradation of indoxacarb in some vegetables and soils has previously been investigated.[4,14−16] However, the degradation and inversion of indoxacarb in different soil conditions, which is important for evaluating its environmental risk, have not been researched. In this study, the enantioselective degradation of indoxacarb was investigated to determine if enantioselectivity occurred in the degradation and conversion processes in acidic as well as alkaline soils. Enantiopure indoxacarb enantiomers were also incubated separately to elucidate the potential racemization of indoxacarb in soil and its influence on the chiral transformation process.

MATERIALS AND METHODS

Chemicals and Materials. The analytical standard of *rac*-indoxacarb (purity = 99.5%) was purchased from Dr. Ehrenstorfer GmbH (Augsberg, Germany). Enantiopure indoxacarb enantiomers were prepared via enantiomeric resolution of racemic indoxacarb by chiral HPLC. In this step, indoxacarb racemate of known quantity was injected into the chiral HPLC system, and the mobile phase fractions corresponding to *R*-(−)- and *S*-(+)-indoxacarb were collected manually by observing their UV signals. The collected samples were then gently evaporated to dryness under a vacuum evaporator and used as enantiomer standards. The enantiopurity of the prepared indoxacarb enantiomers, checked with chiral HPLC using the same column system, was >99%. A stock solution of *rac*-indoxacarb was prepared in hexane and stored at −20 °C. Working standard solutions were prepared by diluting an appropriate amount of the stock solution in hexane and stored at 4 °C.

Acetonitrile, acetone, and sodium chloride were of analytical grade and were purchased from Beijing Chemical Works (Beijing, China). Isopropanol and hexane were of HPLC grade and were purchased from Fisher Scientific (Fair Lawn, NJ, USA). Water was purified by a Milli-Q system. Cleanert Florisil solid phase extraction (SPE) cartridges (1000 mg/6 mL) were purchased from Agela Technologies Inc. (Tianjin, China).

Soil Collection. Two soils representing different pH values and climatic environments were collected from agricultural soil of Guangzhou in southern China and Taian in northern China. Soils were collected from a depth of 0−15 cm with a hand auger, transferred into a single container, and mixed thoroughly. Samples were air-dried, stored in the dark, and sifted through 20-mesh before use. The pH values were measured using a pH meter and a sample soil/water ratio of 1:2.5. The two soils were either slightly acidic or alkaline with pH values of 4.55 and 8.10, respectively. Other soil properties were as follows: Guangzhou soil, organic matter 3.42%, sand 49.25%, silt 32.43%, and clay 18.32%; Taian soil, organic matter 1.12%, sand 31.05%, silt 47.48%, and clay 21.47%. No indoxacarb was found at detectable levels in two soils. When sterilized experiments were performed, the soil, water, and glassware used were autoclaved at 121 °C twice (20 min per time).

Soil Incubation. Separate incubation experiments were conducted with racemic and enantiopure *R*-(−)- and *S*-(+)-indoxacarb. The incubation conditions are given in Table 1. Sterilized control experiments (experiments S1′, S2′, and S3′, respectively, for acidic soil; S4′, S5′, and S6′, respectively, for alkaline soil) were performed and compared to the corresponding nonsterilized experiments. To avoid the potential effects of solvent on the microbiological activity of the soils, a portion of 10 g of dry soil was transferred into a 250 mL conical flask and spiked with 100 μL of stock solution in hexane containing approximately 1.5×10^4 μg of racemic indoxacarb and 2.0×10^4 μg of individual enantiomers. The resulting mixture was stirred for 5 min. The spiked soils were allowed to air-dry for 10 min before the remaining soil (90 g) was mixed thoroughly for another 15 min, yielding fortification levels of 15 and 20 μg/g, respectively (experiments S1, S2, and S3, respectively, for acidic soil; S4, S5, and S6, respectively, for alkaline soil). Soils were incubated with a water content of 20−30 g/100 g of dry soil by adding distilled water. After mixing, the flasks were sealed with cotton−wool plugs and incubated at 25 ± 1 °C in the dark for 75 days. Distilled water was added at 3- or 4-day intervals by weight to maintain the initial moisture. During the incubation, aliquots of 10 g of soil (based on dry weight) were removed from each treatment at different time intervals and frozen at −20 °C until analysis. Soils were collected at 2 h and at 1, 3, 7, 21, 30, 50, and 75 days. Three replicate soil samples were followed at each experiment level.

Table 1. Incubation Conditions for Soil Experiments

expt	soil type	spiked compd	microbial activity
S1	acidic	*rac*-indoxacarb	nonsterilized
S2	acidic	*R*-(−)-indoxacarb	nonsterilized
S3	acidic	*S*-(−)-indoxacarb	nonsterilized
S4	alkaline	*rac*-indoxacarb	nonsterilized
S5	alkaline	*R*-(−)-indoxacarb	nonsterilized
S6	alkaline	*S*-(−)-indoxacarb	nonsterilized
S1′	acidic	*rac*-indoxacarb	sterilized
S2′	acidic	*R*-(−)-indoxacarb	sterilized
S3′	acidic	*S*-(−)-indoxacarb	sterilized
S4′	alkaline	*rac*-indoxacarb	sterilized
S5′	alkaline	*R*-(−)-indoxacarb	sterilized
S6′	alkaline	*S*-(−)-indoxacarb	sterilized

Extraction and Purification of Indoxacarb from Soil. The extraction of indoxacarb from soil was performed according to previous literature.[4] In brief, 10 g soil samples were weighed in a 50 mL polypropylene centrifuge tube with 5 mL of distilled water and 20 mL of acetonitrile. The mixture was shaken vigorously by hand. The tube was then ultrasonicated for 15 min. Five grams of sodium chloride was added to the extract, and the solution was shaken vigorously for 1 min and centrifuged at 3000 rpm for 5 min. An aliquot of supernatant (10 mL) was transferred to a 100 mL round-bottom flask and evaporated to near dryness using a rotatory evaporator under pressure at 35 °C. The residue was dissolved in 2 mL of hexane for cleanup.

The sample extract was decanted to a Florisil SPE cartridge preconditioned with 5 mL of hexane. A mixture of 5 mL of hexane/acetone (9:1, v/v) was used to wash the flask and was then transferred to the cartridge. All of the above solutions were discarded. The mixture of hexane/acetone (9:1, v/v) was added to the cartridge (5 mL × 3 times) to elute analyte and was evaporated to dryness on an evaporator under pressure at 30 °C. The residue was reconstituted with 2.5 mL of hexane. A 20 μL aliquot was injected into the HPLC.

Enantioselective HPLC Analysis. The chromatographic measurements were performed using a Waters (Milford, MA, USA) HPLC system equipped with a 2695 separations module and a 2998 photodiode array detector (PAD). The enantiomers of indoxacarb were separated on a chiral OD-RH column filled with CSP of cellulose-tris(3,5-dimethylphenylcarbamate) (CDMPC) (250 mm × 4.6 mm, 5 μm). The mobile phase was a mixture of hexane/isopropanol (85:15, v/v). The flow rate was 0.8 mL/min. Photodiode array detection was conducted at 310 nm at room temperature.

The enantiomeric elution order was detected on an Agilent 1200 series HPLC equipped with a G1322A degasser, a G1311A quaternary pump, a G1315C diode array detector, and a G1329A autosampler (Wilmington, DE, USA). The left- and right-rotation enantiomers of indoxacarb were confirmed by a CHIRALYSER-MP optical rotation detector produced by IBZ MESSTECHNIK GmbH (Hannover, Germany) and provided by Beijing Separation Science and Technology Development Co., Ltd. (Beijing, China). The optical signals were transformed with an Agilent 35900E A/D converter and processed by Agilent Chemstation. The two enantiomers gave two separate peaks with retention times at 15.87 and 26.49 min for *R*-(−)- and *S*-(+)-indoxacarb under the described conditions. The two enantiomers were separated completely, and there were no interference peaks at their retention times. In addition, soil samples

Table 2. Kinetic Rate Constants k (Day^{-1}) and Half-lives $t_{1/2}$ (Days) for Dissipation of Indoxacarb in Nonsterilized Soil

expt	soil type	spiked compd	detected compd	$k \times 10^{-2}$ (day^{-1})	$t_{1/2}$ (days)	r
S1	acidic	*rac*-indoxacarb	*R*-(−)-indoxacarb	6.64	10.43	0.8587
			S-(−)-indoxacarb	4.95	14.00	0.9138
S2	acidic	*R*-(−)- indoxacarb	*R*-(−)-indoxacarb	18.19	3.80	0.7310
S3	acidic	*S*-(−)- indoxacarb	*R*-(−)- + *S*-(−)-indoxacarb	39.20	1.77	0.9597
S4	alkaline	*rac*-indoxacarb	*R*-(−)-indoxacarb	5.71	12.14	0.9295
			S-(−)-indoxacarb	14.19	4.88	0.9826
S5	alkaline	*R*-(−)- indoxacarb	*R*-(−)- + *S*-(−)- indoxacarb	5.12	13.52	0.6437
S6	alkaline	*S*-(−)- indoxacarb	*R*-(−)- + *S*-(−)-indoxacarb	5.70	12.14	0.5040

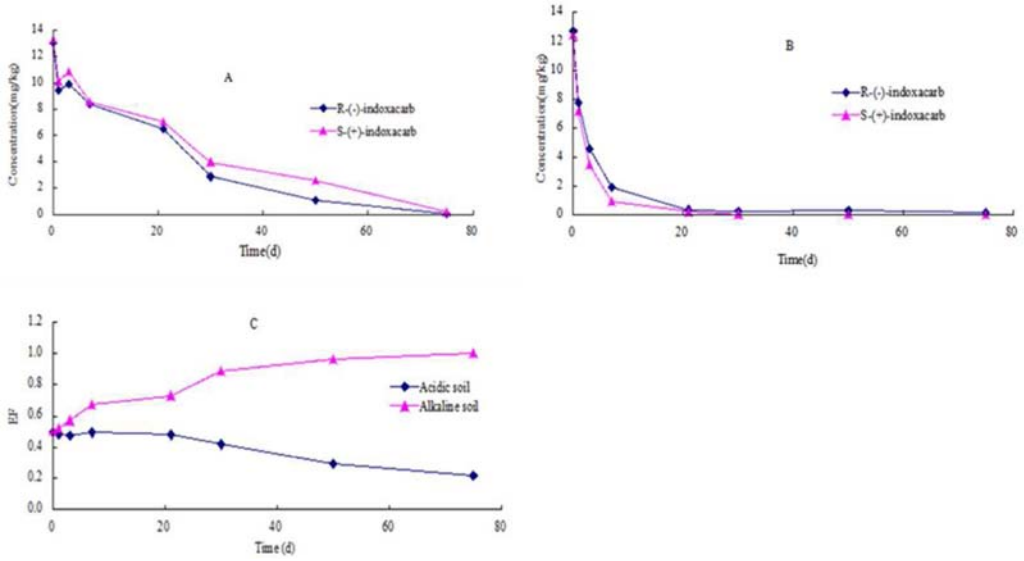

Figure 2. Degradation of *rac*-indoxacarb under nonsterilized conditions in acidic soil (A), alkaline soil (B) and the changes of EF values in two soils (C).

were fortified with enantiopure indoxacarb enantiomers and analyzed immediately. The results showed that no interconversion between enantiomers occurred during the extraction and HPLC separation processes.

A series of blank samples fortified with *rac*-indoxacarb at 0.05, 1, and 5 mg/kg were prepared for method validation and analyzed as described above. Recoveries, which were >89%, were estimated by comparing the peak area of the extracted analyte to that of an equivalent amount of the matrix-matched standard. The limit of detection (LOD), defined as the concentration that produced a signal-to-noise (S/N) ratio of 3, was 0.01 mg/kg. The limit of quantification (LOQ) was 0.05 mg/kg based on an acceptable RSD below 7.4%.

The enantiomeric fraction (EF) was used as a measure of the enantioselective degradation of indoxacarb enantiomers in soil samples. EF is defined by the following equation:

$$EF = A_1/(A_1 + A_2)$$

A_1 and A_2 are the peak areas of *R*-(−)- and *S*-(+)-indoxacarb, respectively. The EF values range from 0 to 1, with EF = 0.5 representing a racemic mixture.

RESULTS AND DISCUSSION

Enantioselective Degradation of Racemic Indoxacarb in Nonsterilized Soils. From experiments S1−S6, the degradation of *rac*-indoxacarb and enantiopure indoxacarb enantiomers followed first-order kinetics. The kinetic data, including the degradation rate constant k and the half-lives $t_{1/2}$, were calculated and are listed in Table 2.

In experiment S1, *R*-(−)-indoxacarb declined more rapidly than *S*-(+)-indoxacarb in acidic soil (Guangzhou pH 4.55) with half-lives 10.43 and 14.00 days, respectively. The half-lives are similar to the results obtained by Li.[14] The enantiomeric concentrations of *R*-(−)- and *S*-(+)-indoxacarb decreased from 13.06 and 13.27 to 0.05 and 0.18 mg/kg, respectively. More than 99% of the spiked indoxacarb enantiomers dissipated after 75 days of incubation, with dissipation rates of 0.0664 and 0.0495 (Table 2).

In experiment S4, the initial concentration of *R*-(−)-indoxacarb was 12.71 mg/kg and decreased to 0.13 mg/kg after 75 days of incubation, with an average dissipation rate of 0.0571 mg/kg per day in alkaline soil (Taian pH 8.10). More than 99% of the initial concentration dissipated. The initial concentration of *S*-(+)-indoxacarb was 12.43 mg/kg, which decreased to 0.01 mg/kg after 50 days of incubation, with an average dissipation rate of 0.1419 (Table 2). On day 75, *S*-(+)-indoxacarb was undetectable, with only *R*-(−)-indoxacarb remaining (Figure 2B). The half-lives of *R*-(−)- and *S*-(+)-indoxacarb in alkaline soil were 12.14 and 4.88 days, respectively. *S*-(+)-Indoxacarb decreased much faster than its antipode, which meant that it might be unstable in alkaline conditions.

The changes in the EF values of the two enantiomers in soils are shown in Figure 2C. In acidic soil, the EF values decreased from 0.51 to 0.22 within 75 days of incubation. In alkaline soil, however, the EF values increased from 0.50 to 1.0 [*S*-(+)-indoxacarb was below the LOQ] during the incubation. Li et al.[14] also studied the enantioselective degradation of indoxacarb in different pH soils. They found that EF values showed no significant changes in acidic soils. However, in

dx.doi.org/10.1021/jf4045952 | J. Agric. Food Chem. 2013, 61, 11273−11277

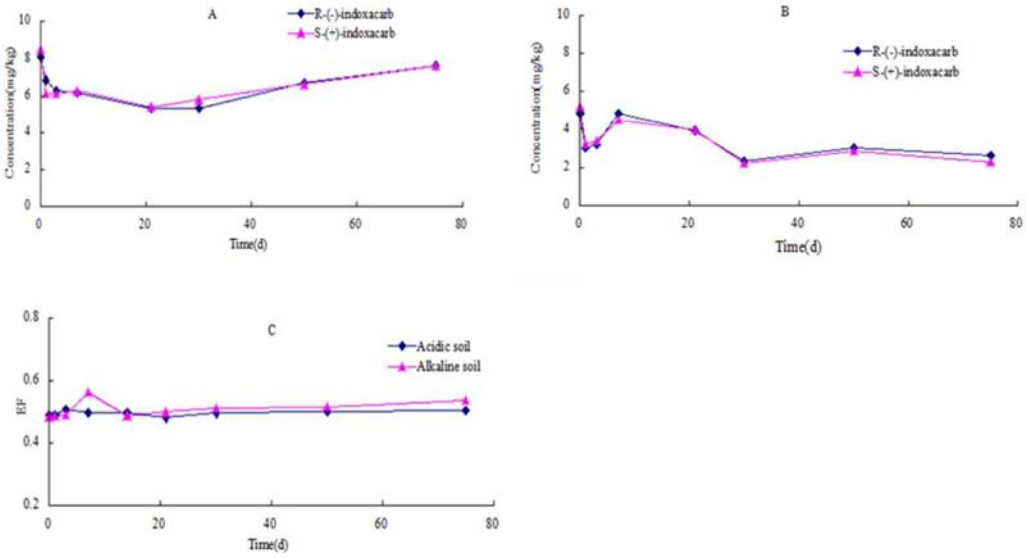

Figure 3. Degradation of *rac*-indoxacarb under sterilized conditions in acidic soil (A), alkaline soil (B) and EF value curves of indoxacarb in two soils (C).

alkaline soil, the EF values increased first and then decreased with time. The different results of the two studies might be explained by the different soils having different pH values and containing different organic matter, microbes, and so on. The different EF value changes of the two soils indicated that *R*-(−)-indoxacarb degraded more quickly in acidic soil, whereas in alkaline soil *S*-(+)-indoxacarb declined more quickly, resulting in enrichment of *R*-(−)-indoxacarb. The changes in EF values in acidic and alkaline soils might be attributable to the activity of microorganisms in these two soils. Different soil types might contain different microbial populations equipped with different enzymes, which are preferential degraders of different enantiomers.[17] Various fungi, bacteria, and actinomycetes have been described to be responsible for the biodegradation pesticide in soils.[18−20] Further studies should be carried out to isolate the special microbial communities that played a key role in the enantioselective degradation of indoxacarb. Additionally, *S*-(+)-indoxacarb declined rapidly in alkaline soil. Therefore, the increase of the EF value in alkaline soil might be the combined effect of microbial and chemical processes.[21,22]

Enantioselective Degradation of Racemic Indoxacarb in Sterilized Soils. In acidic and alkaline sterilized soils (experiments S1′ and S4′), indoxacarb enantiomers showed slow dissipation rates. In acidic soil, the initial concentration of *R*-(−)-indoxacarb was 8.06 mg/kg and decreased to 7.63 mg/kg. Only 5% of the spiked concentration dissipated after 75 days of incubation. For *S*-(+)-indoxacarb, the initial concentration was 8.48 mg/kg and decreased to 7.62 mg/kg after 75 days of incubation, implying a 10% decline of the spiked concentration (Figure 3A). For alkaline soil, the initial concentrations of *R*-(−)- and *S*-(+)-indoxacarb were 4.86 and 5.19 mg/kg, which decreased to 2.64 and 2.28 mg/kg after 75 days of incubation. The spiked concentrations dissipated 46 and 56%, respectively (Figure 3B). This indicated that *S*-(+)-indoxacarb was more prone to degradation than its antipode in these two soils.

It was hypothesized that abiotic factors might have played a greater role in the decline of *S*-(+)-indoxacarb than in *R*-(−)-indoxacarb. By comparison of the results of the non-sterilized and sterilized conditions, it could be concluded that the dissipation of indoxacarb was mainly biologically mediated. However, under sterilized condition, nearly half of the spiked indoxacarb declined, which indicated that there were factors other than microorganisms that caused the enantioselective degradation. According to previous research, indoxacarb is unstable and easily hydrolyzed in alkaline conditions.[23] In this study, the loss of indoxacarb in alkaline soil might be attributed to chemical hydrolysis.

The changes in EF values ranged from 0.49 to 0.50 in acidic soil and from 0.48 to 0.54 in alkaline soil. Overall, small changes in EF values for these two sterilized soil were observed (maintained at 0.5), which meant that little selective degradation occurred (Figure 3C). These results confirmed that biological activity was the main cause of enantioselective degradation in soils.

Degradation of Enantiopure Indoxacarb Enantiomers in Soils. In acidic soil (experiment S2), enantioselective analysis of the soil extracts showed a single peak corresponding to *R*-(−)-indoxacarb prior to the 75 day incubation. The concentration declined rapidly from 14.57 to 0.03 mg/kg within 30 days, with a half-life of 3.80 days. However, for enantiopure *S*-(+)-indoxacarb (experiment S3), the initial concentration was 9.30 mg/kg and decreased to 0.54 mg/kg in 7 days of incubation, with a half-life of 1.77 days. After 7 days, the concentration was below the detectable limit. A peak of *R*-(−)-indoxacarb appeared at 3 days of incubation. The concentration of the *R*-(−)-indoxacarb was measured at 0.22 mg/kg with a conversion rate of 11%. The concentration of *S*-(+)-indoxacarb continued to gradually decrease. This observation suggested that *S*-(+)-indoxacarb was easily converted to *R*-(−)-indoxacarb in alkaline soil, whereas there was no such conversion in acidic soil. The structure of *S*-(+)-indoxacarb might be unstable when it exists alone, and *R*-(−)-indoxacarb could be added in commercial products to maintain the stability of the whole indoxacarb.

Racemization was also observed in the incubation of the two enantiopure enantiomers in alkaline soil (experiment S4 and S5). In alkaline soil, the initial concentrations of *R*-(−)- and *S*-(+)-indoxacarb were 17.83 and 19.04 mg/kg and decreased to 0.32 and 0.14 mg/kg, respectively, on day 75 after incubation.

The half-lives of these two enantiomers were 13.42 and 12.14 days. After 1 day of incubation, 0.17 mg/kg of *S*-(+)-indoxacarb was detected in the enantiopure *R*-(−)-indoxacarb incubation with a conversion rate of 2.0%. For the incubation of *S*-(+)-indoxacarb, 4.51 mg/kg of *R*-(−)-indoxacarb was detected at day 1 of incubation with a conversion rate of 30%. The concentration then gradually decreased with time. The conversion rate of *S*-(+)- to *R*-(−)-indoxacarb was much higher than that of *R*-(+)- to *S*-(−)-indoxacarb in alkaline conditions.

The half-lives of enantiopure enantiomers in acidic soil were much shorter than in alkaline soil, which meant that the enantiomers dissipated easily in acidic conditions when enantiopure enantiomers were incubated. Therefore, it can be concluded that both of the enantiomers were unstable when present in their pure forms, and the tendency to be transformed was from *S*-(+)- to *R*-(−)-indoxacarb in the two conditions studied, which can be explained by the fact that indoxacarb is prone to transform into nontoxic compounds in the environment. The racemization was much faster in alkaline soil compared to acidic soil because indoxacarb is unstable in alkaline conditions.

AUTHOR INFORMATION

Corresponding Authors

*(C.L.) Phone: +86-20-85284925. Fax: +86-20-85284925. E-mail: liuchenglan@scau.edu.cn.
*(B.J.) Phone: +86-23-68349046. Fax: +86-23-68349046. E-mail: jiaobining@cric.cn.

Notes

The authors declare no competing financial interest.

REFERENCES

(1) Harder, H.; Riley, S.; MacCann, S.; Irving, S. DPXMP062: a novel broad-spectrum, environmentally soft, insect control compound. In *Proceedings of the 1996 Brighton Crop Protection Conference*; Sussex, UK, 1996; Vol. 5A-a, pp 449−454.
(2) Dinter, A.; Wiles, J. Safety of the new DuPont insecticide indoxacarb to beneficial arthropods: an overview. *IOBC Bull.* **2000**, *23*, 149−156.
(3) Cheng, L.; Dong, F.; Liu, X.; Chen, W.; Li, Y.; Zheng, Y.; Qin, D.; Gong, Y. Determination of indoxacarb enantiomer residues in vegetables, fruits, and soil by high-performance liquid chromatography. *J. AOAC Int.* **2010**, *93*, 1007−1012.
(4) Sun, D.; Qiu, J.; Wu, Y.; Liang, H.; Li, L.; Liu, C. Enantioselective degradation of indoxacarb in cabbage and soil under field conditions. *Chirality* **2012**, *24*, 628−633.
(5) McCann, S.; Annis, G.; Shapiro, R.; Piotrowski, D.; Lahm, G.; Long, J.; Lee, K.; Hughes, M.; Myers, B.; Griswold, S.; Reeves, B.; March, R.; Sharpe, P.; Lowder, P.; Barnette, W.; Wing, K. The discovery of indoxacarb: oxadiazines as a new class of pyrazoline-type insecticides. *Pest Manag. Sci.* **2001**, *57*, 153−164.
(6) Li, X.; Ma, H.; Gu, L.; Yu, X.; Zhang, H.; Liu, Y.; Xing, Y. Research and comparison of the synthetic routes of indoxacarb. *Mod. Agrochem.* **2009**, *8*, 23−26.
(7) Garrison, A.; Schmitt, P.; Martens, D.; Kettrup, A. Enantiomeric selectivity in the environmental degradation of dichlorprop as determined by high-performance capillary electrophoresis. *Environ. Sci. Technol.* **1996**, *30*, 2449−2455.
(8) Williams, A. Opportunities for chiral agrochemicals. *Pestic. Sci.* **1996**, *46*, 3−9.
(9) Garrison, A. Probing the enantioselectivity of chiral pesticides. *Environ. Sci. Technol.* **2006**, *40*, 16−23.
(10) Ye, J.; Zhao, M.; Liu, J.; Liu, W. Enantioselectivity in environmental risk assessment of modern chiral pesticides. *Environ. Pollut.* **2010**, *158*, 2371−2383.
(11) Diao, J.; Xu, P.; Wang, P.; Lu, Y.; Lu, D.; Zhou, Z. Environmental behavior of the chiral aryloxyphenoxypropionate herbicide diclofop-methyl and diclofop: enantiomerization and enantioselective degradation in soil. *Environ. Sci. Technol.* **2010**, *44*, 2042−2047.
(12) Li, Z.; Zhang, Y.; Li, Q.; Wang, W.; Li, J. Enantioselective degradation, abiotic racemization, and chiral transformation of triadimefon in soils. *Environ. Sci. Technol.* **2011**, *45*, 2797−2803.
(13) Li, Y.; Dong, F.; Liu, X.; Xu, J.; Li, J.; Kong, Z.; Chen, X.; Zheng, Y. Environmental behavior of the chiraltriazole fungicide fenbuconazole and its chiral metabolites: enantioselective transformation and degradation in soils. *Environ. Sci. Technol.* **2012**, *46*, 2675−2683.
(14) Li, X.; Liu, Y.; Liu, S.; Hu, C.; Bai, L.; Gao, B.; Jiang, H. Enantioselective degradation of indoxacarb enantiomers in soils. *Environ. Chem.* **2012**, *31*, 1262−1267.
(15) Wang, H.; Dong, F.; Li, Y.; Chen, X.; Cheng, Y.; Xiang, W.; Zheng, Y. Enantioselective determination of the indecticide indoxacarb in cucumber and tomato by chiral liquid chromatography-tandem mass spectrometry. *Chirality* **2013**, *25*, 350−354.
(16) Jyot, G.; Sahoo, S.; Kaur, S.; Battu, R.; Singh, B. Estimation of indoxacarb residues by QuEChERS technique and its degradation pattern in cabbage. *Bull. Environ. Contam. Toxicol.* **2012**, *88*, 372−376.
(17) Monkiedje, A.; Spiteller, M.; Bester, K. Degradation of racemic and enantiopure metalaxyl in tropical and temperate soils. *Environ. Sci. Technol.* **2003**, *37*, 707−712.
(18) Buerge, I.; Poiger, T.; Müller, M.; Buser, H. Enantioselective degradation of metalaxyl in soils: chiral preference changes with soil pH. *Environ. Sci. Technol.* **2003**, *37*, 2668−2674.
(19) Pai, S.; Riley, M.; Camper, N. Microbial degradation of mefenoxam in rhizosphere of *Zinnia angustifolia*. *Chemosphere* **2001**, *44*, 577−582.
(20) Jones, W.; Ananyeva, N. Correlations between pesticide transformation rate and microbial respiration activity in soil of different ecosystems. *Biol. Fertil. Soils.* **2001**, *33*, 477−483.
(21) Dewey, K.; Gaw, S.; Northcott, G.; Lauren, D.; Hackenburg, S. The effects of copper on microbial activity and the degradation of atrazine and indoxacarb in a New Zealand soil. *Soil Biol. Biochem.* **2012**, *52*, 64−74.
(22) Sarmah, A.; Muller, K.; Ahmad, R. Fate and behaviour of pesticides in the agroecosystem − a review with a New Zealand perspective. *Aust. J. Soil Res.* **2004**, *42*, 125−154.
(23) Ma, J.; Ou, X.; Bu, H.; Cai, D.; Nie, S.; Liang, J. Application of orthogonal experiment in surfactant screening of formulation indoxacarb 10% SC. *Mod. Agrochem.* **2009**, *8*, 15−18.