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Different Enantioselective Degradation of Pyraclofos in Soils

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ABSTRACT: This study investigated the enantioselective degradation behavior of pyraclofos in three soils (NC, HZ, and ZZ) under native and sterilized conditions. The absolute configuration of pyraclofos enantiomers has been determined by the combination of experimental and calculated electronic circular dichroism spectra. *S*-(+)- and *R*-(−)-Pyraclofos were separated and determined on a cellulose tri-(4-chloro-3-methylphenylcarbamate) (Lux Cellulose-4) chiral column by reversed-phase high-performance liquid chromatography−tandem mass spectrometry. Pyraclofos enantiomers were configurationally stable in three soils and no interconversion was observed during the incubation of enantiopure *S*-(+)- or *R*-(−)-pyraclofos under native conditions. The enantioselective degradation behavior of chiral pyraclofos was dramatically different in three soils under native conditions, with half-lives ($t_{1/2}$) of pyraclofos in NC, HZ, and ZZ soils of 2.6, 13.4, and 7.8 days for *S*-(+)-pyraclofos and 9.2, 9.3, and 8.2 days for *R*-(−)-pyraclofos. Compared to the half-lives ($t_{1/2}$) of *rac*-pyraclofos of 21.5, 55.9, and 14.4 days in sterilized NC, HZ and ZZ soils, the degradation velocity was greatly improved in native soils, indicating that degradation was greatly attributed to microbially mediated processes in agricultural cultivating soils.

KEYWORDS: *enantioselectivity, chiral, pyraclofos, soil*

INTRODUCTION

Organophosphorus pesticides (OPs) are extensively employed in modern agriculture. Due to their ability to inhibit acetylcholinesterase, a widely distributed serine esterase, OPs may show high toxicity to nontargeted pests and animals.[1,2] Considering the potential risk of OPs to organisms and microorganisms in the environment, the residues levels and degradation process for OPs in environmental matrices, including soil,[3−6] water,[7,8] and sediment,[9,10] have been widely evaluated. Most OPs contain a chiral center such as carbon, sulfur, pentavalent phosphorus, or other atoms as a substituent of phosphorus.[11] It is well-known that enantiomers of chiral OPs have identical physical and chemical properties; however, they may differ significantly in environmental fate when individual enantiomers interact with other chiral molecules, such as enzymes and biological receptors of microorganism in water or soils. For example, the occurrence of enantioselectivity was observed in two soils with the insecticidally more active (+)-phenthoate degrading faster than its antipode (−)-enantiomer, leading to residues enriched with the less active (−)-phenthoate.[6]

Pyraclofos, (*RS*)-[*O*-1-(4-chlorophenyl)pyrazol-4-yl *O*-ethyl *S*-propyl phosphorothioate], is a special OP because it simultaneously belongs to pesticide and veterinary drug categories. It was first introduced by Takeda (Tokyo, Japan) as Code TIA-230[12] and was registered in many countries and commonly used to control lepidoptera, coleoptera, acarina, and nematodes in fruits, vegetables, and other crops. Pyraclofos was also combined with albendazole to be used as an anthelmintic in sheep.[13] Studies on pyraclofos hydrolysis in buffered solutions and sorption in soils have been reported by Yang et al.[14] However, as a chiral OP with an asymmetric phosphorus atom, very few data related to the pyraclofos enantiomers are available. By using a large amount of surfactants including chiral sodium cholate and achiral sodium dodecyl sulfate, Huang et al.[15] reported that capillary electrophoresis was successfully applied for enantiomeric separation of pyraclofos. Comparison of the degradation process of pyraclofos enantiomers as well as their chiral stability in soils has not been documented. In order to evaluate the enantioselective behavior of two pyraclofos enantiomers in the environment, it is useful to establish the method for separation and determination of pyraclofos residues in soils and provide information related to the enantiomers' degradation behavior in soils.

A direct reversed-phase (RP) chiral assay based on high-performance liquid chromatography−tandem mass spectrometry (HPLC-MS/MS) with high sensitivity and convenience has been applied for the determination of pesticide enantiomer residues, such as famoxadone in spinach,[16] fenbuconazole and myclobutanil in strawberries,[17] and fenbuconazole with its main metabolites in soil and water.[18] In this work, a quick and sensitive method for the determination of pyraclofos enantiomers in soils was also constructed through RP-HPLC-MS/MS. As the assignment of absolute configuration (AC) is of critical importance for understanding the biochemical processing of chiral compounds, the absolute configurations of the pyraclofos enantiomers were determined according to a comparison of experimental and calculated electronic circular dichroism (ECD) spectra. Because the soil properties may have a major impact on the activity of the soil microbial community, which could influence chiral signatures,[19−21] the degradation behavior of pyraclofos enantiomers was investigated in cultivating soils from three geographically different locations

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representing different physicochemical characteristics in China under native as well as sterilized conditions.

MATERIALS AND METHODS

Chemicals and Materials. HPLC-grade methanol and HPLC-grade acetonitrile were purchased from Merck. Two enantiomers of pyraclofos with purity ≥98.0% were obtained from Daicel (Shanghai, China). Formic acid was purchased from Tedia. Silica-based sorbents including C_{18} (40 μm particle size) and primary secondary amine (PSA) (40 μm particle size) were obtained from Agilent. Sodium chloride and anhydrous magnesium sulfate were supplied by Huadong Medicine (China). The chiral analytical column cellulose tris(4-chloro-3-methylphenylcarbamate) (Lux Cellulose-4, 2.0 mm × 150 mm i.d., 3 μm) was purchased from Phenomenex (Torrance, United States).

Circular Dichroism Spectroscopy. ECD spectroscopy was carried out on a Jasco-J815 spectropolarimeter at room temperature. Spectra were collected from 200 to 400 nm with a scan speed of 50 nm/min. A quartz cell with a path length of 0.1 cm was used, and the average of three scans was reported.

Calculations of Electronic Circular Dichroism. The geometry of two pyraclofos enantiomers was first optimized by Gaussian 09 with density functional theory (DFT) at the level of B3LYP/6-31+G*. The ECD calculations of two pyraclofos enantiomers were carried out by Gaussian 09 with time-dependent density functional theory (TDDFT) methods at the level of B3LYP/6-31+G* following reported protocols.[22]

Soil Samples. Three soil samples representing diverse physicochemical properties were collected from a 0−15 cm plow layer from geographically distinct agriculture regions of China (Nanchang in Jiangxi, Hangzhou in Zhejiang, and Zhengzhou in Henan). The level of pyraclofos in these soil samples was lower than the limits of detection (LODs) of the detection method. All samples were air-dried at room temperature, homogenized, passed through a 2-mm sieve, and stored in the dark for several days until use. More details on soil sites and specific physicochemical characteristics (particle size, pH, and organic matter content) are presented in Table 1.

Table 1. Characteristics of Three Soils

	particle size				
soil site	sand (%)	silt (%)	clay (%)	pH (water)[a]	organic matter (g/kg)
Nanchang (NC)	46.55	14.01	39.44	5.08	2.2
Hangzhou (HZ)	66.30	24.03	9.67	6.71	26
Zhengzhou (ZZ)	84.34	4.00	11.66	7.95	13

[a]Suspension of soil in water, 1:2.5 (w/w).

Incubation in Soils under Native Conditions. Separate incubation experiments with the pure *S*-(+)- and *R*-(−) enantiomers and the racemic compounds in soils were conducted in 50-mL polypropylene centrifuge tubes covered with aluminum foil.[23] Approximately 5.0 g of soil (dry weight equivalent) was fortified with 25 μg (50 μL of a 500 μg/mL stock solution in acetone) of *S*-(+)- or *R*-(−)-pyraclofos or 50 μg of racemic pyraclofos (*S*:*R* = 1:1), and they were set to air-dry for 5 min before being homogenized thoroughly (experiments NC1, NC2, and NC3, respectively, for Nanchang soil; HZ1, HZ2 and HZ3, respectively, for Hangzhou soil; and ZZ1, ZZ2, and ZZ3, respectively, for Zhengzhou soil). Then the soil samples were rehydrated by addition of 1.2 mL of deionized water [about 60% of the field holding capacity (w/w)] and incubated at 25 °C in the dark; in order to compensate water loss throughout the experiments, the samples were weighed regularly and deionized water was added to the samples. Three replicate samples were removed from each treatment at different time intervals (0, 0.5, 1, 3, 5, 7, 10, 15, 20, and 25 days) and immediately transferred into a freezer (−40 °C).

Incubation in Soils under Sterilized Conditions. To determine if the enantioselective degradation was a result of microbially mediated transformations, portions of 5.0 g of soil set in 50 mL polypropylene centrifuge tubes were subjected to sterilization treatment, which was achieved by autoclaving the samples twice at 121 °C for 40 min with 24-h intervals to eliminate microbial activity. The sterilized samples were fortified with 50 μg of racemic pyraclofos (*S*:*R* = 1:1, spike level 10 μg/g) (experiments NCS, HZS, and ZZS) and added with sterile water at a biological clean workbench. The samples were then covered with cellophane and kraft paper to maintain sterile conditions.

Extraction of Incubated Soil Samples. Samples were thawed at room temperature and added with 10 mL of water. To extract the pyraclofos residues, 25 mL of acetonitrile, 6 g of anhydrous $MgSO_4$, and 1.5 g of NaCl were added to the samples. Then the tube was stirred on a vortex shaker for 3 min, ultrasonically extracted for 10 min, and centrifuged at 6000 rpm for 5 min. A portion of 1 mL of organic layer was transferred and mixed with 50 mg of PSA, 50 mg of C_{18}, and 150 mg of anhydrous $MgSO_4$ for cleanup. After shaking and centrifugation, the supernatant was diluted to 50% with water for analysis.

Enantioselective HPLC-MS/MS Analysis. HPLC-MS/MS detection was achieved by use of the TSQ quantum mass spectrometer system (Thermo Fisher Scientific) equipped with an electrospray interface. Xcalibur 2.0.7 (Thermo Fisher Scientific) software was used to process the quantitative data obtained from calibration standards and samples. Enantioselective chromatographic separation was performed on a Phenomenex column Cellulose-4. The mobile phase consisted of 55% (v/v) (A) methanol and 45% (v/v) (B) 0.1% formic acid solution. The mobile phase was delivered at a flow rate of 0.25 mL/min in isocratic mode and the injection volume was 5 μL. Electron spray ionization (ESI) was operated in the positive ion mode. Spray voltage was set at 4.2 kV. The capillary temperature was set to 350 °C. Auxiliary gas and sheath gas were normal nitrogen. Collision gas was high pure argon with pressure at 1.5×10^{-3} Torr in the collision cell. Transition m/z 361 → 138 was used for quantification, and m/z 361 → 257 and 361 → 275 were used for confirmation.

Method Validation. The solvent calibration curve for each pyraclofos enantiomer was obtained by plotting peak areas of quantification ion transition against analyte concentrations from 0.2 to 1000 μg/L with regression analysis. To evaluate the matrix effect, the matrix matched calibration curves of pyraclofos enantiomer in the range from 0.2 to 1000 μg/L were also constructed for each soil sample. The linearity was expressed as correlation coefficient. The LODs were determined as 3 times the signal-to-noise ration of the quantitative ion transition in soils as well as the limits of quantitation (LOQs), determined as 10 times.

Method accuracy and precision were evaluated by recovery studies using spiked samples at four concentration levels (0.005, 0.05, 0.5, and 5.0 μg/g for each pyraclofos enantiomer based on five replicates). For method recovery studies, samples

without residue (5.0 g) were spiked prior to extraction by the addition of appropriate volumes of the pesticide standard solution in acetone. Recoveries of these compounds were determined immediately after fortification. The precision of the method was determined by the repeatability and reproducibility studies and expressed as relative standard deviation (RSD). The repeatability, RSD_r, was measured by comparing the SD of the recovery percentage of spiked samples run on the same day. The reproducibility, RSD_R, was determined by analyzing spiked samples from three different days.

Kinetics Analysis. The kinetic study of pyraclofos in soil was performed by plotting residue concentration against time, and the maximum squares of the correlation coefficients were used to determine the equations of the best-fitting curves. For all samples studied, exponential relations were found to apply, corresponding to first-order rate equations. The corresponding rate constant k is determined from the linear plots of logarithmic transformation of [C] versus time t in eq 1:

$$\ln[C] = \ln[C]_{t=0} - kt \quad (1)$$

where [C] are the concentrations of *S*-(+) and *R*-(−) enantiomers at time t, and k are the degradation rate constants of *S*-(+)- and *R*-(−) enantiomers, respectively. If degradation is enantioselective ($k_S \neq k_R$), the enantiomer ratio (ER) could be expressed as a function of time (t) in eq 2 or 3:

$$ER_t = [S]/[R] = ER_0 e^{\Delta kt} \quad (2)$$

$$\ln(ER_t) = \ln(ER_0) + \Delta kt \quad (3)$$

where ER_0 is the initial ER value and Δk is the difference between k_S and k_R, which reflects the rate at which ER deviates from ER_0 over time.

RESULTS AND DISCUSSION

Absolute Configuration Assignment of Pyraclofos Enantiomers. Assignment of the absolute configuration of chiral molecules is critical for chiral analysis. Chiroptical methods such as vibrational circular dichroism (VCD) and ECD have been widely employed in determination of the ACs of chiral molecules with the aid of computational methods. In this paper, we applied the TDDFT methodology to calculate the ECD spectra of pyraclofos. Through the combination of experimental and computated ECD spectra, the absolute configuration of pyraclofos enantiomers was finally assigned.

The individual enantiomers of pyraclofos were stereochemically analyzed by CD spectroscopy and almost mirror-imaged CD curves were provided. The overall curves of computed ECD obtained by TDDFT calculations (Figure 1A) and experimental ECD (Figure 1B) are highly similar. By comparison to the absolute configurations from computed ECD, we can correctly assign the configurations of pyraclofos enantiomers eluted from the columns. On the basis of computed ECD, the enantiomers with peaks 1 and 2 of Figure 1B and Figure 2A are assigned as *S*-(+)- and *R*-(−)-pyraclofos, respectively.

Method Validation. Using m/z 361 → 138 as quantification transition, the solvent and matrix matched calibration curves were linear from 0.2 to 1000 μg/L for each pyraclofos enantiomer, with correlation coefficients higher than 0.994. No significant matrix effect in soil samples was found, as the relative difference between the slopes of solvent and matrix matched calibration curves was less than 5%. For two enantiomers, the recoveries obtained were in the acceptable range of 76.3−97.2%, the repeatability RSD_r ranged from 3.4% to 10.2%, and the reproducibility RSD_R ranged from 6.0% to 12.1% (seen in Table 2). The LODs were 0.0006 μg/g and LOQs were 0.002 μg/g for each pyraclofos enantiomer.

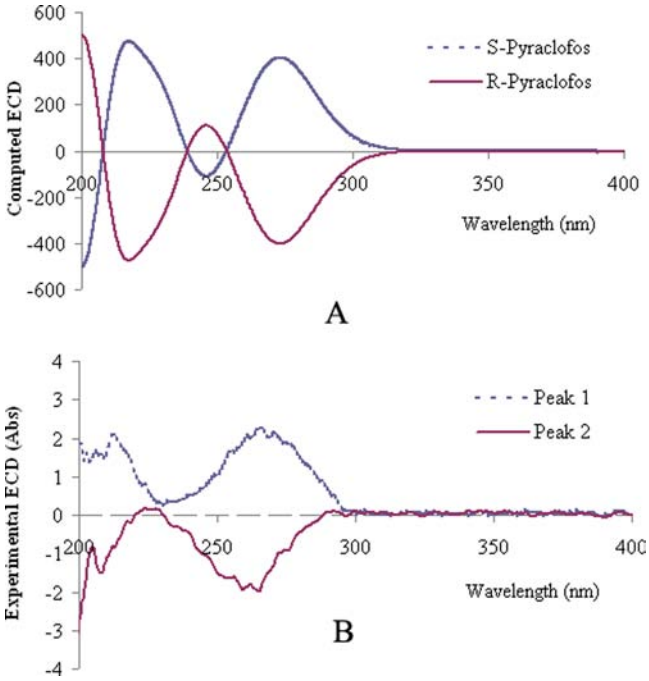

Figure 1. (A) Calculated and (B) experimentally measured ECD spectra of pyraclofos enantiomers in acetonitrile (1 μg/mL).

Degradation of Pyraclofos in Three Soils under Sterilized Condition. No significant enantioselectivity for pyraclofos degradation in three soils under sterilized condition was found. In Figure 2A, no obvious difference is seen between the peak areas of *S*-(+)- and *R*-(−) enantiomers in NCS experiments after incubation for 25 days under sterilized conditions. In Figure 3 we plotted the data from experiments NCS, HZS, and ZZS, and the results of the kinetics study of pyraclofos residue in three soils showed that pyraclofos degradation coincided with $C = 9.596e^{-0.0323t}$ for NCS, $C = 9.077e^{-0.0124t}$ for HZS, and $C = 9.218e^{-0.0483t}$ for ZZS. The half-lives ($t_{1/2}$) of racemic pyraclofos in three soils (NC, HZ, and ZZ) were about 21.5, 55.9, and 14.4 days.

The pH may have an important role during compound degradation in sterilized soils. It has been reported that pyraclofos is relatively stable in both acidic and neutral buffers, and it was readily hydrolyzed under basic conditions.[14] In this sterilized experiment the degradation time $t_{1/2}$ in ZZ soil (pH, 7.95) was 14.4 days, relatively shorter than those in the NC (pH 5.08) and HZ soils (pH 6.71), which may prove pyraclofos is easier to degrade in alkaline matrix.

Enantioselective Degradation of Pyraclofos in Three Soils under Native Condition. During the degradation of enantiopure *S*-(+)- or *R*-(−)-enantiomer in native soils, no interconversion of *S*-(+)- to *R*-(−) enantiomer and vice versa was detected, and it was demonstrated that the enantiomer was configurationally stable in these three soils. The chromatograms of experiments NC1 and NC2 after 25 days of incubation are shown in Figure 2B,C as an example. The plot of ln [C] from experiments NC1−2, HZ1−2 and ZZ1−2 [incubation of *S*-(+)- or *R*-(−)-pyraclofos in soils] versus incubation time t showed a linear relationship (seen in Figure 4 A−C). The half-life of *S*-(+)-pyraclofos was 2.6, 13.4, and 7.8 days in experiments

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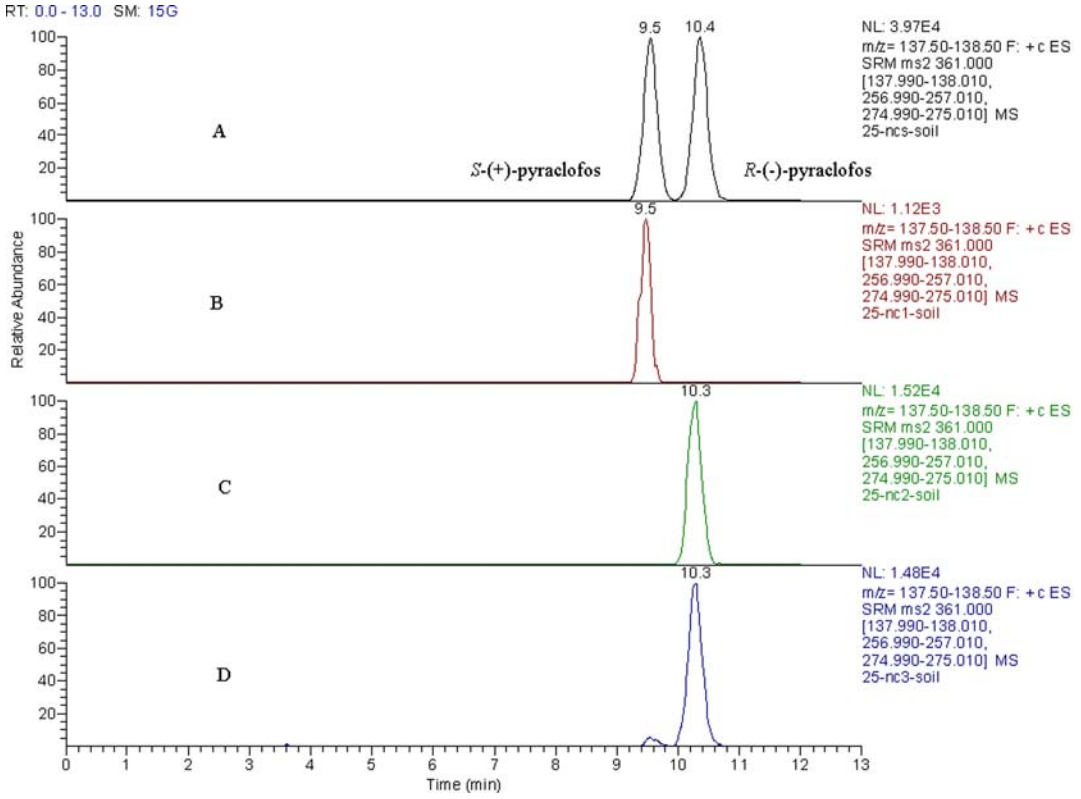

Figure 2. Extracted ion chromatograms of pyraclofos enantiomers in experiments (A) NCS, (B) NC1, (C) NC2, and (D) NC3 after incubation for 25 days.

Table 2. Recovery, RSD_r, and RSD_R Values Obtained for Pyraclofos Enantiomers in Soils at Four Spiked Levels (n = 5)

	AR (%),[a] RSD_r							
	day 1		day 2		day 3		RSD_R	
fortified level (mg/kg)	*S*	*R*	*S*	*R*	*S*	*R*	*S*	*R*
0.005	76.3, 10.8	80.1, 9.8	82.7, 10.0	86.7, 6.8	78.6, 8.7	83.1, 10.2	8.9	12.1
0.05	83.5, 7.4	86.7, 10.5	87.6, 5.9	90.9, 8.2	80.8, 9.4	85.4, 5.8	7.2	9.5
0.5	90.5, 6.2	93.7, 8.4	90.2, 6.6	95.1, 6.0	82.5, 8.3	87.7, 6.1	6.7	9.1
5.0	93.7, 5.0	88.2, 4.7	96.5, 5.4	97.2, 5.9	90.4, 6.1	94.2, 3.4	6.0	7.9

[a]AR, average recoveries.

NC1, HZ1, and ZZ1, and the half-life of *R*-(−)-pyraclofos was 9.2, 9.3, and 8.2 days in experiments NC2, HZ2, and ZZ2, respectively.

The enantiomer ratio (ER = [*S*]/[*R*]) values from *rac*-pyraclofos degradation in three soils under native condition are listed in Table 3, and the plot of ln ER from experiments NC3, ZZ3, and HZ3 (incubation of *rac*-pyraclofos in soils) versus incubation time t showed a linear relationship (seen in Figure 4D). The ERs from the incubation of *rac*-pyraclofos in NC soil showed a continuous decrease with time from an initial value of 1.00 to 0.01 (concentration $S < R$). A plot of ln ER versus time t was linear and the slope indicated a rate difference of 0.191 day^{-1}, which was in agreement with the data ($k_S - k_R$ = 0.2663 − 0.0751 = 0.1912, seen in Figure 4A) . A t-test between the ER values of the spiked soil and ER_0 = 1.00 yielded $p < 0.01$ at the first day and $p < 0.001$ at the third, fifth, seventh, 10th, 15th, 20th, and 25th days. All of them indicated that the degradation of pyraclofos was highly enantioselective in NC soil. The results of much higher *R*-(−)- than *S*-(+) enantiomers in experiment NC3 after incubation for 25 days under native conditions is shown in Figure 2D. In HZ soil samples, the ERs from the incubation of *rac*-pyraclofos showed a continuous

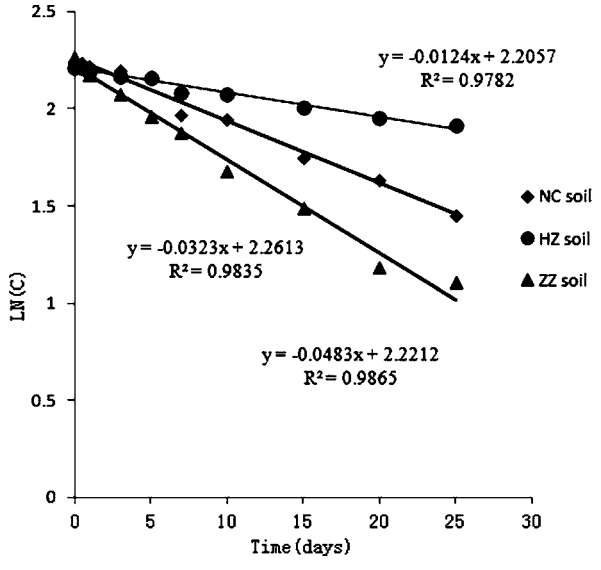

Figure 3. Plot of ln [C] of racemic pyraclofos from experiments NCS, HZS, and ZZS versus incubation time t, showing a linear relationship.

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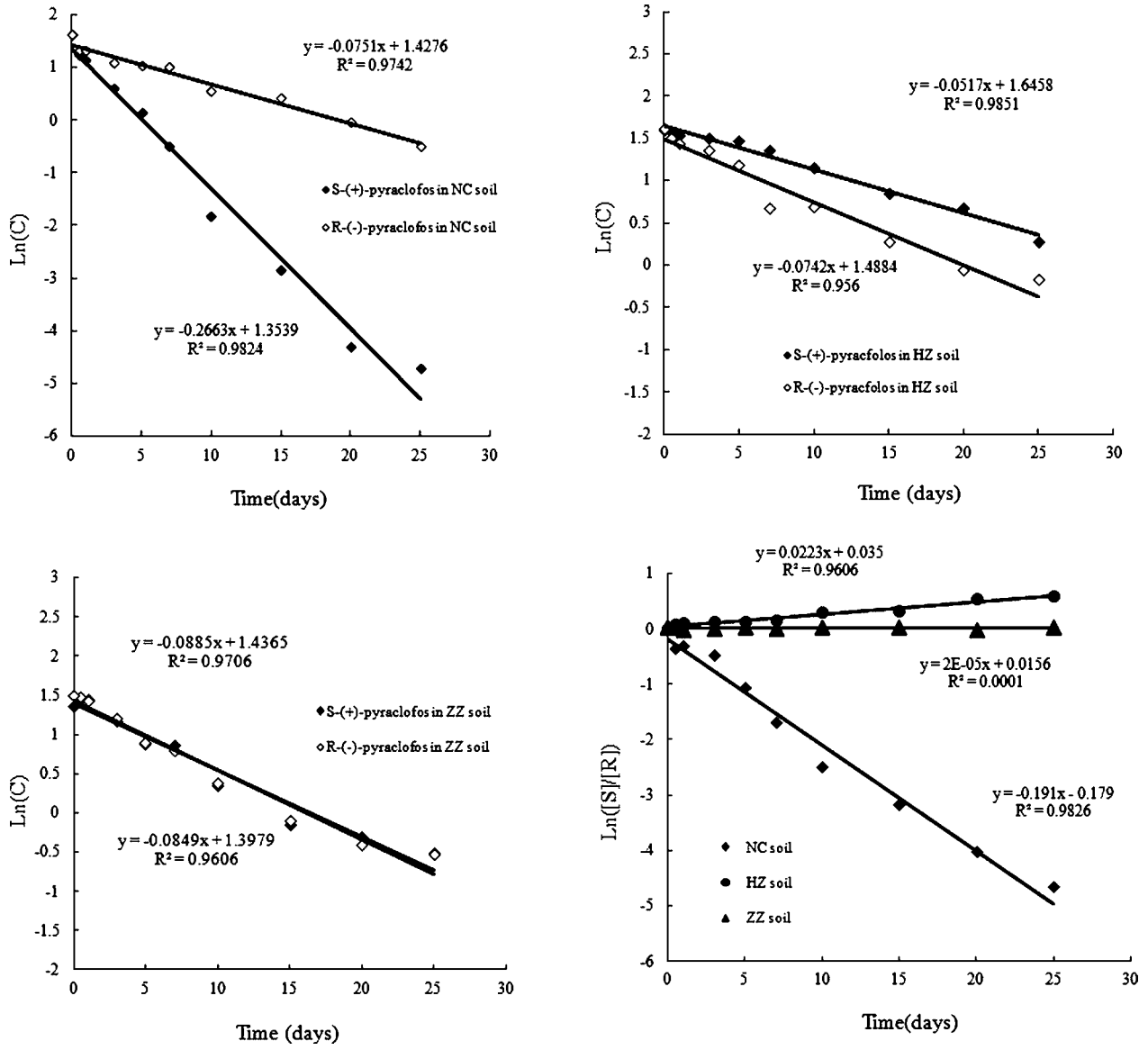

Figure 4. (A–C) Plot of ln [C] from experiments NC1–2, HZ1–2, and ZZ1–2 [incubation of *S*-(+)- or *R*-(−)-pyraclofos] versus incubation time *t*, showing a linear relationship. (D) Plot of ln ER (where ER = [*S*]/[*R*]) from experiments NC3, HZ3, and ZZ3 (incubation of *rac*-pyraclofos) versus incubation time *t*, showing a linear relationship.

Table 3. Enantiomer Ratio of *rac*-Pyraclofos in Experiments NC3, HZ3, and ZZ3 under Native Conditions (n = 3)

	ER (= [*S*]/[*R*])		
time (days)	NC3	HZ3	ZZ3
0	1.00 ± 0.02	0.99 ± 0.06	1.04 ± 0.02
0.5	0.99 ± 0.03	1.09 ± 0.03	1.02 ± 0.03
1	0.85 ± 0.04	1.10 ± 0.04	0.99 ± 0.03
3	0.62 ± 0.02	1.12 ± 0.03	1.01 ± 0.06
5	0.41 ± 0.03	1.13 ± 0.06	1.02 ± 0.08
7	0.22 ± 0.01	1.16 ± 0.08	1.01 ± 0.04
10	0.09 ± 0.01	1.33 ± 0.07	1.02 ± 0.03
15	0.04 ± 0.005	1.38 ± 0.02	1.03 ± 0.02
20	0.02 ± 0.003	1.71 ± 0.06	0.99 ± 0.05
25	0.01 ± 0.001	1.78 ± 0.05	1.03 ± 0.07

increase with time from an initial value of 0.99 to 1.78 (concentration $S > R$). A plot of ln ER versus time t was linear and the slope indicated a rate difference of −0.0223 day^{-1}, which agreed with the data ($k_S - k_R$ = 0.0517 − 0.0742 = −0.0225, seen in Figure 4B). A t-test between the ER values of the spiked soil and ER_0 = 0.99 yielded $p < 0.05$ at the third, fifth, and seventh days; $p < 0.01$ at the 10th and 15th days; and $p < 0.001$ at the 20th and 25th days. All of them indicated that the degradation of pyraclofos was significantly enantioselective in the HZ soil. The ERs from the incubation of *rac*-pyraclofos in the ZZ soil were close to 1.00 and no significant stereoselectivity was shown after the t-test.

The degradation velocity of pyraclofos in each sterilized soil was much slower than that in native soils. It was implied that beside the abiotic degradation of pyraclofos, a main degradation of pyraclofos was attributed to the transformation catalyzed by the microbial community in agricultural soils. No enantioselective behavior was shown under sterilized conditions; however, there was opposite enantioselective behavior for the degradation of pyraclofos enantiomers in the NC and HZ soils. The different enantioselectivity in NC and HZ soils demonstrated that the microorganism activity responsible for the degradation of

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S-(+)-pyraclofos enantiomer prevailed over that for the degradation of *R*-(−)-enantiomer in NC soil, and it was opposite in HZ soil. The active microorganism responsible for the degradation of each pyraclofos enantiomer will be investigated in our future work. The difference in degradation behavior of chiral pyraclofos in soils from different agricultural cultivating areas could provide more information to evaluate environmental and ecological risks of chiral pesticides.

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Notes

The authors declare no competing financial interest.

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