

## RESEARCH ARTICLE

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# Enantioselectivity in degradation and ecological risk of the chiral pesticide ethiprole

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## Abstract

Intensive agricultural activities have caused land degradation due to soil pollution, particularly by pesticides. However, the degradation, metabolism, and toxicity of chiral pesticides by soil microorganisms are often enantioselective. This study aimed to determine the effect of chirality on the degradation of the enantiomers of ethiprole in soil and their impact on soil microbial communities. (*R*)-ethiprole underwent directional chiral conversion to the (*S*)-enantiomer in a paddy soil microcosm, leading to elevated concentrations of (*S*)-ethiprole. Initially, the bacterial operational taxonomic units significantly decreased after 3 days of incubation with *rac*-ethiprole, (*R*)-ethiprole, and (*S*)-ethiprole but gradually increased in the later stage. Principal coordinate analysis revealed that the bacterial community structure was enantioselectively affected by the ethiprole enantiomers. Within 3 days, both *rac*-ethiprole and (*R*)-ethiprole reshaped the original stochastic microbial community into a deterministic community (variable selection). Thus, we propose that the enantioselective behavior and ecotoxicology of chiral pesticides need to be considered, especially because there are numerous chiral pesticides currently in use within agricultural management. The comprehensive understanding of the ecological risk of chiral pesticide enantiomers is vital to the process of improving sustainable production and environmental health in agricultural ecosystems.

## KEYWORDS

bacterial community, chiral ethiprole, ecological risk, enantioselective degradation, paddy soils

## 1 | INTRODUCTION

Land degradation due to pesticide pollution in agricultural soils is a widespread problem that affects human and environmental health, as well as future land use (Deary, Ekumankama, & Cummings, 2018; X. G. Liu,

Dong, Xu, Yuan, & Zheng, 2014). About 19.4% of cultivated land and 11.4% of fallow land in China are polluted by heavy metals, nutrients, and organic pollutants such as pesticides and polycyclic aromatic hydrocarbons (Chen, de Sherbinin, Ye, & Shi, 2014; Rey et al., 2017; Zhao, Luo, Deng, & Yan, 2008). Contamination of soil by pesticides is primarily

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caused by source pollution in cultivated lands and to some extent by non-point source pollution due to long-range atmospheric deposition (Epple, Maguhn, Spitzauer, & Kettrup, 2002; Potter & Coffin, 2017). In recent decades, pesticide use in cultivated land grew due to an increase in global food demand. In 2017, approximately  $1.8 \times 10^6$  and  $3.9 \times 10^5$  tons of pesticides were applied in China and the United States, respectively (de Albuquerque, Carrão, Habenschus, & de Oliveira, 2018). However, it is estimated that the amount of pesticides reaching the target pests is less than 0.1% of the pesticide applied and the rest enters the environment (Pimentel, 1995). Therefore, pesticide pollution may adversely affect the structure and function of soil microbial communities in agricultural fields. Soil microbes play a critical role in global element cycling, as well as mediating transformation of organic matter through those processes, including the degradation of xenobiotics and mineralization of plant nutrients. (Bowles, Acosta-Martínez, Calderón, & Jackson, 2014; Zhao et al., 2016). Hence, the need for systematic evaluation of pesticides on the effects of microbial communities in various soil types.

Approximately 30% of pesticides in current use are chiral, of which 93% are marketed as a racemic mixture (Garrison, 2011; Ye, Zhao, Niu, & Liu, 2015). Furthermore, enantiomers of chiral compounds often exhibit stereoselectivity in chiral environments such as biological systems or chiral surfaces (de Albuquerque et al., 2018; Maia, Ribeiro, Castro, & Tiritan, 2017; Sanganyado, Lu, Fu, Schlenk, & Gan, 2017). For example, (*R*)-metalaxyl (Masbou, Meite, Guyot, & Imfeld, 2018), (*R*)-fenprothrin (P. Zhang et al., 2017), and (*S*)-dufulin (K. K. Zhang, Hu, Zhu, Yang, & Song, 2014) preferentially degraded in soil resulting in enantiomeric enrichment of their antipodes. Furthermore, stereoselectivity has also been observed in the adsorption of chiral compounds on agricultural soil, which may affect their bioavailability for plant uptake, microbial degradation, and transformation (Gámiz, Facenda, & Celis, 2016; Hazen & Sholl, 2003). Hence, switching from racemic mixtures to single enantiomer pesticides is probably preferable when the enantiomer with the highest efficacy is less toxic to nontarget organisms, as well as less persistent in soil.

The enantioselective behavior of chiral pesticides is closely related to soil properties, including pH, organic matter content, and incubation conditions (Buerge, Poiger, Müller, & Buser, 2003, 2006; Frková et al., 2016; X. Wang et al., 2013). For example, (*S*)-methamidophos was preferentially degraded in soil obtained from Zhengzhou but was enriched in soils from Changchun and Nanchang (X. Wang et al., 2013). Furthermore, inversion of one enantiomer to its antipode has been observed in some soil samples probably due to microbial activity (Han, Kitagawa, Wzorek, Klika, & Soloshonok, 2018); for example, (*R*)- and (*S*)-malathion interconverted (Sun et al., 2012) and (*S*)-haloxyfop converted to (*R*)-haloxyfop (Poiger, Müller, Buser, & Buerge, 2015). Hence, it is essential to understand the role of microbial communities in the stereoselective environmental behavior of chiral pesticides in different soils. However, previous studies showed that intensive agricultural activities and increased pesticide cause a reduction in microbial diversity and populations (Fang, Lian, Wang, Cai, & Yu, 2015). However, the effect of chiral pesticides on soil microbiome (especially with regard to microbial biomass and activity) is often overlooked due to complexities of microbe-soil and chiral interactions. Therefore, there is a need to determine the effect of pesticide chirality on bacterial communities as it affects the function and structure of the agricultural ecosystem.

Ethiprole is a broad spectrum phenylpyrazole insecticide with an asymmetric sulfur atom, existing as (*R*)- and (*S*)-enantiomers and applied as a racemic mixture. It exerts its toxicological effects by blocking the passage of chloride ions through GABA ( $\gamma$ -aminobutyric acid) receptors in the central nervous system and is effective against pests in paddy soils (Moffat, 1993). There is a lack of systematic studies on the stereoselective degradation of ethiprole and its impact on soil microbial communities. In this study, the mechanisms of enantioselective behavior of ethiprole in five latitudinal paddy rice soils with different organic matter content and pH values were investigated. High-throughput sequencing technologies were used to determine microbial community changes (here, focus on bacterial community) following exposure to chiral ethiprole and its enantiomers. This study aims to establish the correlations between enantioselective degradation of ethiprole and microbial community. Those results have significant implications for the prediction of potential risks of chiral pesticides to agricultural ecosystems and public health.

## 2 | MATERIALS AND METHODS

### 2.1 | Overview

The details of the experimental approach, including ethiprole-spiking procedures, extraction in soil, and chiral analysis, can be found in Q. Zhang et al. (2016). Briefly, the incubation experiment was conducted over a 180-day period in soil microcosms. Five types of soil samples (top 10-cm layer) were collected from different latitudinal in the main paddy rice sites in China (Ji Lin, Nan Jin, Jiang Xi, Guang Dong, and Hai Nan). The samples were air dried, sieved (2-mm mesh), and stored at 4°C. The properties of the five types of soils were analyzed using established methods (Xiong et al., 2017), and soil properties were described in Table S1. No ethiprole enantiomers were detected in any of the soil samples. Sterilized soils were used in the soil microcosms experiment after spiking with *rac*-ethiprole, (*R*)-ethiprole, or (*S*)-ethiprole in triplicate (Table S2). For each soil microcosm, 20.0-g soil (dry weight) was spiked with 0.1 ml of acetone containing either 800.0  $\mu\text{g}$  of racemic ethiprole or 400.0  $\mu\text{g}$  of individual enantiomers in a 500-ml conical flask. The samples were thoroughly stirred for 10 min. It was ensured that the acetone was adequately evaporated to avoid adverse effects on microbiological activity. An additional 380.0-g nonsterilized soil was added and mixed thoroughly, yielding a final concentration of racemic ethiprole or individual enantiomers of 2.0 or 1.0  $\mu\text{g g}^{-1}$ , respectively. All soils were maintained at a 20.0% moisture content and incubated at 25°C in the dark to facilitate activation of soil microorganisms. Soil incubations containing only deionized water as control were performed to further understand the impact of chiral ethiprole on soil microbial diversity. At selected time intervals (2 hr, 1, 3, 7, 14, 21, 30, 45, 60, 90, 120, 150, 180 days), triplicate 20.0-g soil aliquots from each treatment were randomly removed and were immediately transferred to a -80°C freezer.

### 2.2 | Enantioselective degradation

Equivalent 10.0-g soil samples were extracted with 5.0 ml of distilled water and 50.0 ml of acetonitrile in 100-ml centrifuge tubes. Each

tube was shaken vigorously for 4 min before undergoing sonication extraction for 15 min. The water was removed with the addition of 4.0 g of anhydrous magnesium sulfate ( $\text{MgSO}_4$ ) and 2.0 g of sodium chloride (NaCl). The chemicals and materials used for extraction are described in Method S1. The mixture was vortexed vigorously and then centrifuged at 4,000 rpm for 3 min. The supernatant acetonitrile (25 ml) was collected and completely evaporated. The clean-up method of these soil extracts was performed according to an existing research protocol using a Florisil solid phase extraction column (Q. Zhang et al., 2016; Q. Zhang, Zhang, et al., 2018). The ethiprole residue was then redissolved in 1 ml of methanol and water solution (65:35, v/v). After filtration through a 0.22- $\mu\text{m}$  filter membrane, the soil extracts were analyzed on a chiral Lux Cellulose-2 by Agilent 1200 HPLC system (Agilent, USA) using a mixture of methanol and water (65:35, v/v) as the mobile phase at a flow rate of 0.7 ml  $\text{min}^{-1}$ . The UV detection was performed at 225 nm with a chiral column temperature at 35°C. The recoveries and limit of detection are shown in Method S2. Stereoselectivity was determined using the enantiomeric fraction (EF) and the enantiomeric ratio (ER), as well as over time using  $\Delta k$  (Method S3).

The degradation and chiral conversion ( $S \rightarrow R$ ) rate constants were determined based on first-order processes defined by the following equations (Poiger et al., 2015):

$$d[S]/dt = k_{RS} \times [R] - k_{\text{deg}} \times [S], \quad (1)$$

$$d[R]/dt = k_{SR} \times [S] - k_{\text{deg}} \times [R], \quad (2)$$

where  $k_{\text{deg}}$ ,  $k_{RS}$ , and  $k_{SR}$  are the degradation and chiral conversion rate constants. The  $k_{R\text{-deg}}$  and  $k_{S\text{-deg}}$  values were determined in pure (R)- or (S)-enantiomer incubation experiments by fitting the total concentrations of ethiprole to incubation time in soil.

## 2.3 | Microbial community analysis

### 2.3.1 | DNA extraction, PCR amplification, and Illumina sequencing

Three technical replicates of each soil (0.5 g) sample were used to extract total DNA through the MoBioPowerSoil™ DNA Isolation Kit (Mo Bio Laboratories Inc., Carlsbad, CA, USA) according to the manufacturer's instructions. The concentration and quality of the extracted DNA were determined using NanoDrop ND-2000 spectrophotometry (NanoDrop Technologies, Wilmington, DE). The primer set that consisted of 520F (50-AYTGGGYDTAAAGNG-30) and 802R (50-TACNVGGGTATCTAATCC-30) was used for amplification of V4 hypervariable regions of the bacterial 16S rRNA gene (approximately 254 bp; Xiong et al., 2017). The Polymerase Chain Reaction (PCR) thermal cycling conditions were performed according to previous research methods, with a total of 25 cycles were used to amplify bacterial templates (Xiong et al., 2017; Yang & Ji, 2015). The PCR products were purified by a PCR Purification Kit (Axygen Bio, USA) and were pooled at a concentration of 10 ng  $\mu\text{l}^{-1}$  before sequencing. Paired-end sequencing of bacterial amplicons was used a MiSeq Reagent Kit v3 (Illumina, USA) and performed on the Illumina MiSeq sequencer at Personal Biotechnology Co., Ltd (Shanghai, China).

### 2.3.2 | Bioinformatics and statistical analyses

After removing the adaptors and primer sequences, we assigned the raw sequences to each sample based on the unique barcode provided by QIIME (Caporaso et al., 2010). The split sequences of each sample were merged with FLASH V1.2.7 (Magoč & Salzberg, 2011). The retained sequences of each sample were processed following the established UPARSE pipeline (Edgar, 2013). In addition, the lower quality score (<0.5) and short length sequences (<200 bp) were removed. Then, the remaining sequences were assigned to operational taxonomic units (OTUs) with 97% similarity threshold. The chimera sequences were deserted, and the representative sequences were matched against the Ribosomal Database Project (RDP) database (Cole et al., 2009; Q. Wang, Garrity, Tiedje, & Cole, 2007) using the naive Bayes classifier implemented in Mothur with an 80% confidence threshold (Schloss et al., 2009).

A principal coordinate analysis (PCoA) based on Bray-Curtis distance was performed to explore the differences in bacterial community structures between all soil samples. To examine the enantioselective influence on bacterial OTUs by chiral enantiomers ((R)-, (S)-, and *rac*-ethiprole) in comparison with control treatment (sterilized water). The indicator species analysis (Dufrière & Legendre, 1997) was conducted using "indval" function from the "labdsv" package in R program (version 3.2.2). The OTUs table was rarefied for each sample in different treatments. Samples from the retained OTU table were rarefied to 5,507 sequences for the subsequent analysis, and the reads from each sample ranged from 5,507 to 22,783 in the original OTU table. The OTUs with reads less than 10 were deleted for the indicator species. The indicator species plot was finally visualized with Cytoscape 3.5.1 (Shannon et al., 2003). Moreover, the abundance-weighted  $\beta$ -mean nearest taxon distance ( $\beta\text{MNTD}$ ) was used to determine and quantify community phylogenetic turnover. The  $\beta$ -nearest taxon index ( $\beta\text{NTI}$ ) was further used to quantify the magnitude and direction of a deviation between an observed  $\beta\text{MNTD}$  value and the null  $\beta\text{MNTD}$  distribution (Dini-Andreote, Stegen, van Elsland, & Salles, 2015). A  $|\beta\text{NTI}| > 2$  indicates significant deviation following the dominance of deterministic processes, which includes homogeneous ( $\beta\text{NTI} < -2$ ) and variable selection ( $\beta\text{NTI} > 2$ ). When the  $|\beta\text{NTI}| < 2$ , stochastic processes are dominant (Dini-Andreote et al., 2015; Stegen, Lin, Konopka, & Fredrickson, 2012; Zhou et al., 2013).

## 2.4 | Statistical analysis

Spearman's rank correlation coefficients between the indicator species (OTUs) and the (S)- and (R)-ethiprole degradation rate, as well as the enantioselective behavior of ethiprole in (R)- and *rac*-ethiprole treatment, were calculated by SPSS v20.0 (SPSS Inc., USA).

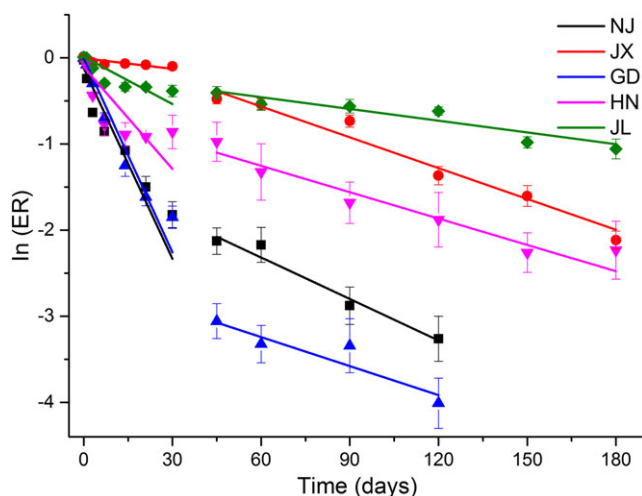
## 3 | RESULTS AND DISCUSSION

### 3.1 | Enantioselective degradation of ethiprole in paddy rice soils

The degradation of ethiprole fitted well with the first-order kinetic model. The half-lives of ethiprole ranged from 55.44 to 76.15 days in

all the five paddy rice soils (Figure S1). (*R*)-ethiprole was not detectable after 150 days of incubation in Nan Jing and Guang Dong paddy rice soils, but (*S*)-ethiprole was detected at concentrations up to 16.4% and 28.1% of the spiked concentration after 180 days of incubation, respectively (Figure S1). The decrease of EF was rapid at the beginning of incubation in four of the paddy rice soils (Nan Jing, Guang Dong, Hai Nan, Ji Lin). The EF value of Jiang Xi soil was still close to 0.50 at 0–30 days but decreased to 0.02 after 180 days of incubation following a rapid degradation. The average EF value ranged from 0.50 to 0.00 in five paddy rice soils at the end of incubation (Figure S2). The initial rapid increase in EF was probably due to chiral inversion that occurred in the first 21-day period. The concentration of (*S*)-ethiprole increased after incubation in all soil samples, except the soil from Jiang Xi (Figure S1). The maximum concentration of (*S*)-ethiprole ranged from 1.1 to 1.5  $\mu\text{g g}^{-1}$  after 7 days (Hai Nan and Ji Lin) and 21 days (Guang Dong and Nan Jing). A detailed discussion of the potential causes of the observed phenomenon is discussed in the next section.

The logarithmic enantiomeric enrichment ( $\ln(\text{ER})$ ) of ethiprole during microbial degradation over time showed two separate lines, with good correlation coefficients ranging from 0.8304 to 0.9835 (Method S3). The slope of these lines is detailed in Table S3. The linear correlation of  $\ln(\text{ER})$  over time consisted of two stages: a rapid decrease that lasted up to 30 days and a slow decrease that extended to 180 days in four of the paddy rice soils (Figure 1). The slope of the first stage was 3.86–6.70 times greater than that of the second stage for ethiprole in four of the paddy rice soils (Nan Jing, Guang Dong, Hai Nan, and Ji Lin). Ethiprole converted to the (*S*)-enantiomer that is more resistant to microbiological degradation; hence, microbial degradation after the 30-day period was slower. A similar trend was observed in the enantioselective degradation of insecticides cis-bifenthrin and cis-permethrin in sediment (W. Liu, Gan, Schlenk, & Jury, 2005). However, the reverse phenomenon was observed in Jiang Xi soils, with the first stage being 2.9 times slower than the second stage. The soil microorganisms in Jiang Xi probably required a period of adjustment before the metabolism of ethiprole commenced; hence, the observed initial time lag. A short lag period suggests that the observed



**FIGURE 1** The regression of enantiomeric ratio (ER) for chiral ethiprole with incubation time in five paddy rice soil at two different phases [Colour figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

enantioselective degradation was probably mediated by soil microorganisms (Lao & Gan, 2012). It is possible that the long-term presence of ethiprole induces the corresponding microbial populations and enantiomer-specific enzymes (Dong et al., 2012; Yang & Ji, 2015). Therefore, the properties of soil and associated microbial communities have a substantial impact on the enantiomeric composition of chiral ethiprole in the soil.

### 3.2 | Directional chiral conversion of ethiprole in soils

For the racemic ethiprole incubation experiments, the final concentrations of (*S*)-ethiprole were shown to be higher than the spiked concentration (Figure S1). To further understand the possible enantioselective degradation, as well as the chiral conversion of chiral insecticides, enantiopure (*R*)-ethiprole was incubated in Ji Lin soil. In this experiment, (*R*)-ethiprole was gradually degraded in paddy rice soil, followed by the appearance of (*S*)-ethiprole. Moreover, the formation of (*S*)-ethiprole increased steadily to a maximum and then maintained a stable concentration until the end of the incubation period. Around 18.9% of (*R*)-ethiprole was converted to (*S*)-ethiprole after 30 days, and the EF decreased from an initial value of 1 to 0.417. In experiment  $S_7$  (soil incubated with (*S*)-ethiprole), (*S*)-ethiprole was configurationally stable, and no formation of the (*R*)-enantiomer was detected (Figure S3). Only (*R*)-ethiprole converted to its antipode leading to a higher concentration of the (*S*)-enantiomer (Figure S3). The  $\ln(\text{ER})$  value over time in the (*R*)-ethiprole incubation experiment was similar to the *rac*-ethiprole incubation, marked by a rapidly decreasing phase followed by a slowly decreasing phase. The  $\Delta k$  for the first phase was 4.1 times greater than that of the later phase for (*R*)-ethiprole in Ji Lin soil. Based on  $\Delta k$  for those two phases, it was further confirmed that ethiprole becomes more resistant to degradation by soil microorganisms over more extended time periods.

The racemization and directional chiral conversion masks the different degradation and conversion rates for individual enantiomers as well as the environmental behavior of chiral compounds (Khan, 2014; Poiger et al., 2015). The degradation and conversion model of ethiprole enantiomers in soil is shown in Figure S4. The degradation and conversion for pure ethiprole enantiomers were determined based on the conceptual model shown in Table 1. According to the incubation experiments  $S_5$ ,  $S_6$ , and  $S_7$  (soil incubated with *rac*-ethiprole, (*R*)-ethiprole, and (*S*)-ethiprole, respectively), the degradation rate ranged from 0.0107 to 0.0118 with a standard deviation of 0.005–0.008, indicating that the degradation rate did not significantly differ among (*R*-), (*S*-), and *rac*-ethiprole incubations through a two-tailed paired *t* test with a probability of 95%. Consequently, the degradation of ethiprole was not enantioselective in the soils tested. The conversion of (*R*-) to (*S*)-ethiprole ( $k_{RS}$ ) apparently compensated for any degradation of (*S*)-ethiprole that occurred. As a result, the concentration of the (*S*) isomer was always higher than that of the (*R*) isomer in the soil samples examined. The rate constants for the conversion of (*R*-) to (*S*)-ethiprole ( $k_{RS}$ ) were 1.76–2.05 times greater than the degradation rate constants of (*S*)-ethiprole ( $k_{deg}$ ) in the phase from 0 to 7 days, whereas the values

**TABLE 1** Degradation and chiral conversion rate constants of ethiprole incubation with *rac*-ethiprole and the pure enantiomers by the kinetic scheme

Spiked compounds	$k_{\text{deg}}$ (day <sup>-1</sup> )	Phase I (0–7 days) $k_{RS}$ (day <sup>-1</sup> )	Phase II (14–180 days) $k_{RS}$ (day <sup>-1</sup> )	$k_{R-S}$ (day <sup>-1</sup> )
<i>rac</i> -ethiprole	0.0118 ± 0.0005	0.0243 ± 0.0026	0.00403 ± 0.0006	0.0049 ± 0.0005
( <i>R</i> )-ethiprole	0.0114 ± 0.0007	0.0201 ± 0.0047	0.00289 ± 0.0003	0.0034 ± 0.0003
( <i>S</i> )-ethiprole	0.0107 ± 0.0008	-	-	-

Note.  $k_{\text{deg}}$ ,  $k_{RS}$  and  $k_{SR}$  values were fitted for each experiment individually in JL soil.

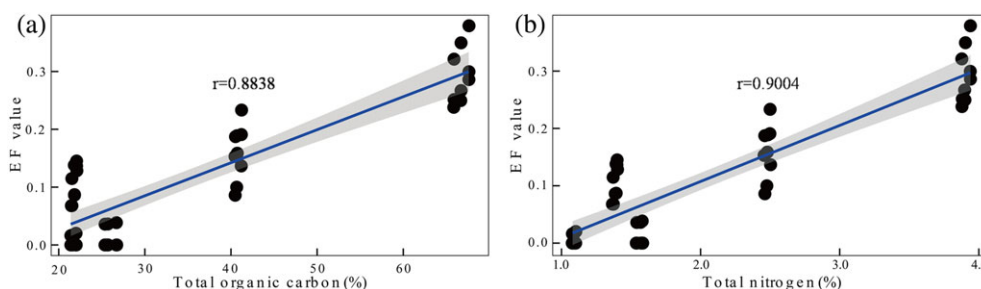
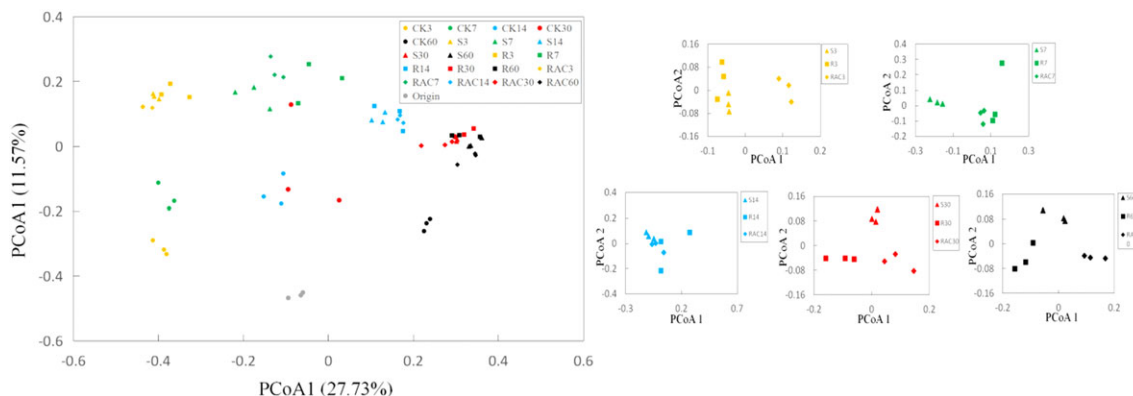
of the rate constant  $k_{RS}$  were 2.93–3.94 times slower than the degradation rate constants in the phase from 14 to 180 days. The average conversion rate constants ( $k_{RS}$ ) were 2.40–3.35 times slower than the degradation rate constants of (*S*)-ethiprole ( $k_{\text{deg}}$ ) over the whole period, resulting in a gradual decrease in (*S*)-ethiprole later in the incubation process.

The results suggest that there was a unidirectional chiral inversion of (*R*)-ethiprole to (*S*)-ethiprole. Ethiprole is a chiral sulfoxide ( $R_1S(O)R_2$  ( $R_1 \neq R_2$ )); however, previous studies have shown that thermal, photochemical, or chemical processes can cause chiral inversion in chiral sulfoxides through processes such as pyramid atomic inversion (Jenks, Matsunaga, & Gordon, 1996; Marom, Biedermann, & Agranat, 2007). Furthermore, a study on flosequinan, a chiral sulfoxide quinolone vasodilator, demonstrated that bidirectional chiral inversion is probably mediated by microbes (Eiji, Tsuyoshi, Takashi, Masaaki, & Tetsuya, 1994). The mechanism of chiral inversion involved

stereoselective reduction of (*R*)- or (*S*)-flosequinan by gut microbes to form a sulfide, which was subsequently oxidized to produce the antipode (Eiji et al., 1994). Therefore, because the soil microcosm was kept in darkness and the temperature was similar for all treatments, chiral inversion of (*R*)-ethiprole was probably caused by an interaction with chemical constituents of the different soil samples or microbial activity. Furthermore, chiral inversion was not observed in the sterilized soil microcosms.

### 3.3 | Correlation between the enantioselective behavior of ethiprole and soil properties

The correlation between the enantioselective behavior of ethiprole and soil properties was statistically analyzed based on five different regions of soil amended with *rac*-ethiprole. When the EF of the last

**FIGURE 2** The regression of enantiomeric fraction (EF) values for chiral ethiprole in soils with five different nutrient contents at the stable stage (from 120 to 180 days) [Colour figure can be viewed at wileyonlinelibrary.com]**FIGURE 3** Bray–Curtis dissimilarity principal coordinate analysis (PCoA) of bacterial community structures exposed to different chiral ethiprole enantiomers at different times (0, 3, 7, 14, 30, and 60 days). The soils were separately amended with pure (*R*)-, (*S*)-, or *rac*-ethiprole [Colour figure can be viewed at wileyonlinelibrary.com]

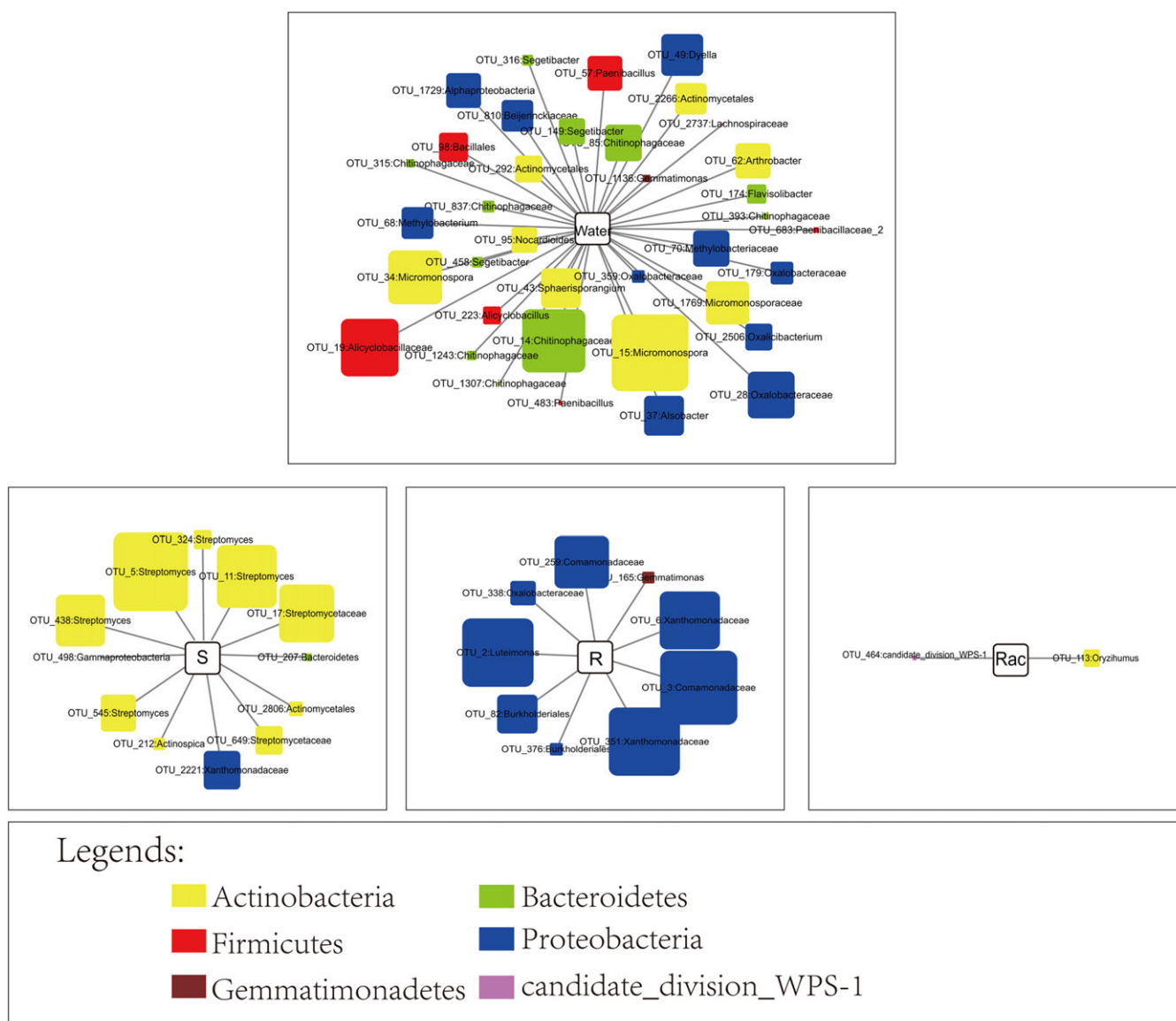
three time points (120, 150, and 180 days) was plotted against various soil parameters, the percentage of total organic carbon and soil nitrogen content shows a good relationship with the EF, with correlation coefficients ( $r$ ) of up to 0.8838 and 0.9004, respectively (Figure 2). However, the enantioselective behavior of ethiprole did not significantly correlate with other soil parameters. The soils with high percentages of total organic carbon and high nitrogen content caused microorganisms to transform (*R*)-ethiprole to (*S*)-ethiprole. The (*S*)-enantiomer was not detectable in Jiang Xi soil, which had lower concentrations of total organic carbon and nitrogen. The microorganisms which transformed (*R*)-ethiprole to the (*S*)-enantiomer probably proliferated in high carbon and nitrogen soils. Previous studies suggested organic matter promotes pesticide degradation by providing carbon sources for the soil microbial growth (Qi et al., 2016; Z. Zhang, Gao, et al., 2018). However, high organic matter content may decrease the degradation rate because more pesticides will adsorb to the soil organic matter and become less available for

contacting with soil microbes (Qi et al., 2016). Because stereoselectivity was not observed in sterilized treatments, chiral inversion in soils with high organic matter was probably caused by the increase in microbial activity and growth. Therefore, the enantioselectivity of ethiprole has a close relationship with the presence of soil the nutrients.

### 3.4 | Effects of ethiprole on soil microbial community

#### 3.4.1 | Enantioselective changes in soil bacterial community

Soil samples were incubated after treatment them with different ethiprole enantiomers to show the effect of chiral ethiprole on soil microbial community. Figure S5 shows the bacterial OTUs number for different chiral ethiprole enantiomers treatment in different times (0, 3, 7, 14, 30, and 60 days). The bacterial OTUs number significantly



**FIGURE 4** The indicator species of operational taxonomic units (OTUs) for different treatments (soils are amended with water, pure (*R*)-, (*S*)-, or *rac*-ethiprole). Nodes represent different OTUs, and node sizes correspond to their average relative abundance (log transformation) across all the samples [Colour figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

decreased after incubation with sterile water, (S)-, (R)-, and *rac*-ethiprole, and the bacterial OTUs number are shown lowest after 3 days of incubation. And then the bacterial OTUs number gradually increased in the later incubation stage. The overall taxonomic complexity of the microbial community at the bacterial phylum level is presented in Figure S6. *Proteobacteria*, *Actinobacteria*, and *Firmicutes* were the predominant bacterial phyla present, accounting for 75.38% of the total bacterial sequences. *Firmicutes* decreased gradually with incubation time suggesting the chiral ethiprole restricted the relative abundance of *Firmicutes* in the soil. Conversely, *Gemmatimonadetes* steadily increased over the period studied and was probably activated in the presence of chiral ethiprole. In contrast, *Firmicutes* was stimulated to grow, and *Gemmatimonadetes* restricted when soils were treated with a novel neonicotinoid insecticide called paichongding (Cai et al., 2016). These results suggest that the same bacterial phylum were influenced differently by exposure to different pesticides and different enantiomers of chiral pesticides.

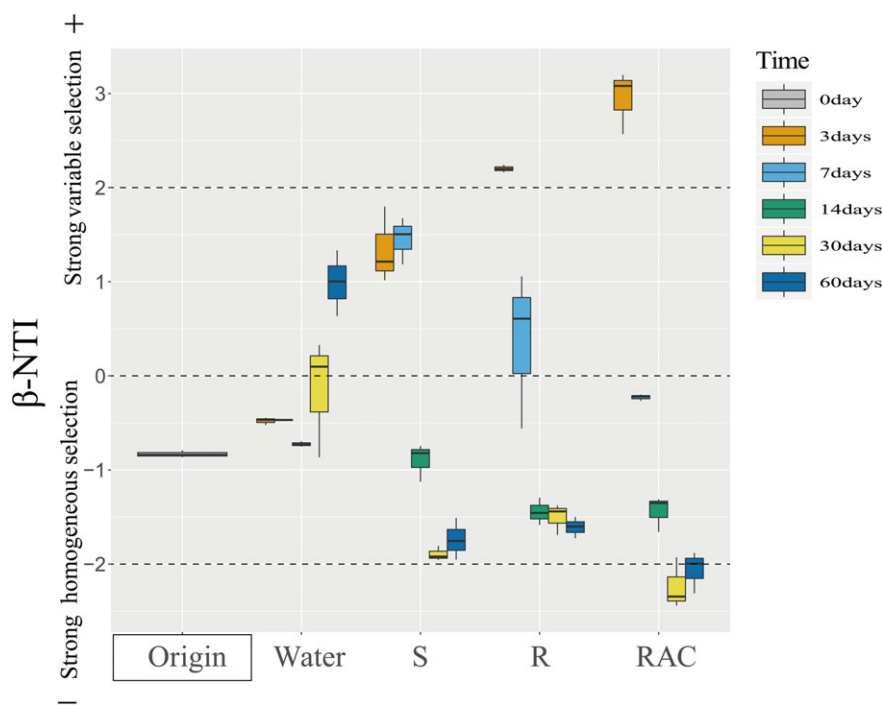
As shown in Figure 3, Bray–Curtis dissimilarity PCoA indicated that bacterial structure showed the most pronounced differences between applied chiral ethiprole soil and untreated soil. As shown by the PCoA1, the incubation time influenced bacterial community structures in all the treatment (treatment with (R)-, (S)-, and *rac*-ethiprole). The results show that the structure of soil bacterial communities was affected by the presence of ethiprole enantiomers and their incubation time. This suggests that chiral enantiomers may cause significant effects on microbial community structures and may lead to different ecological risks in contaminated regions of the environment.

### 3.4.2 | Indicator species by the treatment of chiral ethiprole

The indicator species of bacterial OTUs are used to assess the efficacy of chiral ethiprole in agricultural management (Hartmann, Frey, Mayer, Mader, & Widmer, 2015; Siddig, Ellison, Ochs, Villar, & Lau, 2016; Sun

et al., 2016). Indicator species (OTUs) for the bacteria present in soils amended with different chiral enantiomers are shown in Figure 4. The control soil samples amended with water contain extremely abundant indicator species, and they mainly included *Actinobacteria*, *Bacteroidetes*, *Firmicutes*, and *Proteobacteria*. The higher relative abundances of indicator species in (S)-ethiprole amended soil samples were OTU5, 11, 17, and 438, all belonging to the phylum *Actinobacteria*. The relative abundances of these four OTUs have good positive correlations with the degradation and chiral conversion rates of ethiprole in Ji Lin soils, with correlation coefficients ranging from 0.464 to 0.968 (Table S4). (S)-ethiprole may serve as a carbon and nitrogen source for some bacteria because the relative abundances of some bacteria within the groups *Streptomyces* and *Paenibacillus* were decreased with decreased concentrations of (S)-ethiprole in the soil.

Almost all the indicator species belonged to *Proteobacteria* in the (R)-ethiprole soil samples. The indicator species with the highest relative abundances were from the groups *Luteimonas*, *Comamonadaceae*, and *Xanthomonadaceae* (OTU2, 3, 6, 259, and 351), all of which showed a negative correlation with the degradation and chiral conversion rate of (R)-ethiprole with correlation coefficients ranging from  $-0.293$  to  $-0.839$  (Table S4). The relative abundances of the indicator species decreased at higher concentrations of (R)-ethiprole in the soil. Hence, the chiral conversion of (S)-ethiprole to its antipode influenced these bacterial OTUs. A soil microcosm study found that soil samples treated with (R)-imazethapyr had the lowest diversity compared whereas (S)-imazethapyr-treated samples appeared to be more diverse based on Shannon's and Simpson's diversity indices (Qian et al., 2015). However, the presence of *rac*-ethiprole caused massive reductions of indicator species, with only OTU113 (*Oryzihumus*) and 464 (candidate division WPS-1) observed in paddy rice soil following ethiprole addition. Therefore, the ecological and toxicological impact of *rac*-ethiprole on bacterial communities will probably create a higher ecological risk in agriculture fields.



**FIGURE 5** The dynamic patterns of  $\beta$ -nearest taxon index ( $\beta$ -NTI) distributions of bacterial community succession for different chiral ethiprole enantiomers in agricultural soil. Horizontal dashed lines indicate upper and lower significance thresholds at  $\beta$ -NTI =  $-2$  and  $+2$ , respectively [Colour figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

### 3.5 | Enantioselectivity in microbial assembly

The application of agricultural pesticides in farming systems is increasing the importance of deterministic selection in ecological succession. The  $\beta$ NTI value in water treated and (S)-ethiprole treated soils showed that the stochastic processes ( $-2 < \beta$ NTI  $< +2$ ) were dominant throughout the time series (Figure 5). The  $\beta$ NTI values in soil incubated with *rac*-ethiprole and (*R*)-ethiprole revealed microbial assembly distribution progressively shifted with increasing incubation time, from initially being stochastic community assembly ( $-2 < \beta$ NTI  $< 2$ ) to subsequently being a deterministic selection (variable selection;  $\beta$ NTI  $> 2$ ) within 3 days. The soil incubation with (*R*)-ethiprole restored stochastic community assembly ( $-2 < \beta$ NTI  $< 2$ ) from 7 to 60 days (Dini-Andreote et al., 2015). The soil incubation with *rac*-ethiprole restored stochastic community assembly ( $-2 < \beta$ NTI  $< 2$ ) from 7 to 14 days and then transitioned to deterministic selection (homogeneous selection;  $\beta$ NTI  $< -2$ ) after 30 days (Dini-Andreote et al., 2015). (*R*)-ethiprole and *rac*-ethiprole had a strong driving effect on bacterial community succession in the soil. Therefore, it appears that only one enantiomer may be expected to contribute significantly to the ecological effects for some chiral insecticides. This knowledge will contribute to a complete understanding of ecological effects caused by the application of chiral pesticides.

## 4 | CONCLUSION

The present outcomes indicate that the enantioselective behavior and ecological effects of the chiral phenylpyrazole insecticide ethiprole occurred concurrently in a simulated agricultural ecosystem. (*R*)-ethiprole was readily converted to the (*S*) isomer in paddy soils resulting in (*S*)-ethiprole occupying a higher percentage of total ethiprole in agricultural fields. Enantioselectivity for ethiprole shows a close relationship with the presence of soil nutrients, (i.e., total organic carbon and nitrogen). Therefore, different enantioselectivity occurs for chiral pollutants depending on the application of various fertilizers, such as organic fertilizer, which may be effective in reducing the concentrations of highly toxic chiral enantiomers in agricultural systems (Mueller & Buser, 1995). Moreover, the selective conversion of chiral ethiprole proliferated within the groups *Luteimonas*, *Comamonadaceae*, and *Xanthomonadaceae* in bacteria. This information is conducive to the development of chiral pharmaceuticals and pesticides with a short half-life, high bioactivity, and low ecological toxicity. Importantly, the chiral ethiprole enantiomers exert dramatically different influences on soil microbial community structures and ecological succession in agroecosystems (Hawkesworth & García Pérez, 2003). Therefore, we propose that the enantioselective behavior and resultant ecotoxicology of chiral pesticides need to be considered in pesticide registration before the application of a chiral pesticide in agricultural systems. Our results reveal a potential implication for environmental protection and ecosystem service. The comprehensive understanding of chiral pesticide fate is aimed at reducing the concentrations of high-risk chiral pesticide enantiomers and improving sustainable production in agroecosystems.

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## REFERENCES

- Bowles, T. M., Acosta-Martínez, V., Calderón, F., & Jackson, L. E. (2014). Soil enzyme activities, microbial communities, and carbon and nitrogen availability in organic agroecosystems across an intensively-managed agricultural landscape. *Soil Biology and Biochemistry*, *68*, 252–262. <https://doi.org/10.1016/j.soilbio.2013.10.004>
- Buerge, I. I., Poiger, T., Müller, M. D., & Buser, H.-R. (2003). Enantioselective degradation of metalaxyl in soils: Chiral preference changes with soil pH. *Environmental Science and Technology*, *37*, 2668–2674. <https://doi.org/10.1021/es0202412>
- Buerge, I. J., Poiger, T., Müller, M. D., & Buser, H. R. (2006). Influence of pH on the stereoselective degradation of the fungicides epoxiconazole and cyproconazole in soils. *Environmental Science and Technology*, *40*, 5443–5450. <https://doi.org/10.1021/es060817d>
- Cai, Z., Ma, J., Wang, J., Cai, J., Yang, G., & Zhao, X. (2016). Impact of the novel neonicotinoid insecticide Paichongding on bacterial communities in yellow loam and Huangshi soils. *Environmental Science and Pollution Research*, *23*, 5134–5142. <https://doi.org/10.1007/s11356-015-5733-7>
- Caporaso, J. G., Kuczynski, J., Stombaugh, J., Bittinger, K., Bushman, F. D., Costello, E. K., ... Knight, R. (2010). QIIME allows analysis of high-throughput community sequencing data. *Nature Methods*, *7*, 335–336. <https://doi.org/10.1038/nmeth.f.303>
- Chen, R., de Sherbinin, A., Ye, C., & Shi, G. (2014). China's soil pollution: Farms on the frontline. *Science*, *344*, 691–691. <https://doi.org/10.1126/science.344.6185.691-a>
- Cole, J. R., Wang, Q., Cardenas, E., Fish, J., Chai, B., Farris, R. J., ... others (2009). The Ribosomal Database Project: Improved alignments and new tools for rRNA analysis. *Nucleic Acids Research*, *37*, 141–145. <https://doi.org/10.1093/nar/gkn879>
- de Albuquerque, N. C. P., Carrão, D. B., Habenschus, M. D., & de Oliveira, A. R. M. (2018). Metabolism studies of chiral pesticides: A critical review. *Journal of Pharmaceutical and Biomedical Analysis*, *147*, 89–109. <https://doi.org/10.1016/j.jpba.2017.08.011>
- Deary, M. E., Ekumankama, C. C., & Cummings, S. P. (2018). Effect of lead, cadmium, and mercury co-contaminants on biodegradation in PAH-polluted soils. *Land Degradation & Development*, *29*, 1583–1594. <https://doi.org/10.1002/ldr.2958>
- Dini-Andreote, F., Stegen, J. C., van Elsas, J. D., & Salles, J. F. (2015). Disentangling mechanisms that mediate the balance between stochastic and deterministic processes in microbial succession. *Proceedings of the National Academy of Sciences*, *112*, E1326–E1332. <https://doi.org/10.1073/pnas.1414261112>
- Dong, F., Cheng, L., Liu, X., Xu, J., Li, J., Li, Y., ... Zheng, Y. (2012). Enantioselective analysis of triazole fungicide myclobutanil in cucumber and soil under different application modes by chiral liquid chromatography/tandem mass spectrometry. *Journal of Agricultural and Food Chemistry*, *60*, 1929–1936. <https://doi.org/10.1021/jf204762t>
- Dufrêne, M., & Legendre, P. (1997). Species assemblages and indicator species: The need for a flexible asymmetrical approach. *Ecological Monographs*, *67*, 345–366. [https://doi.org/10.1890/0012-9615\(1997\)067\[0345:SAAI\]2.0.CO;2](https://doi.org/10.1890/0012-9615(1997)067[0345:SAAI]2.0.CO;2)
- Edgar, R. C. (2013). UPARSE: Highly accurate OTU sequences from microbial amplicon reads. *Nature Methods*, *10*, 996–998. <https://doi.org/10.1038/nmeth.2604>
- Eiji, K., Tsuyoshi, Y., Takashi, T., Masaaki, O., & Tetsuya, K. (1994). Chiral inversion of drug: Role of intestinal bacteria in the stereoselective



- sulphoxide reduction of flosequinan. *Biochemical Pharmacology*, 48, 237–243. [https://doi.org/10.1016/0006-2952\(94\)90093-0](https://doi.org/10.1016/0006-2952(94)90093-0)
- Epple, J., Maguhn, J., Spitzauer, P., & Kettrup, A. (2002). Input of pesticides by atmospheric deposition. *Geoderma*, 105, 327–349. [https://doi.org/10.1016/S0016-7061\(01\)00111-2](https://doi.org/10.1016/S0016-7061(01)00111-2)
- Fang, H., Lian, J., Wang, H., Cai, L., & Yu, Y. (2015). Exploring bacterial community structure and function associated with atrazine biodegradation in repeatedly treated soils. *Journal of Hazardous Materials*, 286, 457–465. <https://doi.org/10.1016/j.jhazmat.2015.01.006>
- Frková, Z., Johansen, A., de Jonge, L. W., Olsen, P., Gosewinkel, U., & Bester, K. (2016). Degradation and enantiomeric fractionation of mecoprop in soil previously exposed to phenoxy acid herbicides—New insights for bioremediation. *Science of the Total Environment*, 569–570, 1457–1465. <https://doi.org/10.1016/j.scitotenv.2016.06.236>
- Gámiz, B., Facenda, G., & Celis, R. (2016). Evidence for the effect of sorption enantioselectivity on the availability of chiral pesticide enantiomers in soil. *Environmental Pollution*, 213, 966–973. <https://doi.org/10.1016/j.envpol.2016.03.052>
- Garrison, A. W. (2011). An introduction to pesticide chirality and the consequences of stereoselectivity. *Chiral Pesticides: Stereoselectivity and Its Consequences*. American Chemical Society, 1. DOI: <https://doi.org/10.1021/bk-2011-1085.ch001>
- Han, J., Kitagawa, O., Wzorek, A., Klika, K. D., & Soloshonok, V. A. (2018). The self-disproportionation of enantiomers (SDE): A menace or an opportunity? *Chemical Science*, 9, 1718–1739. <https://doi.org/10.1039/c7sc05138g>
- Hartmann, M., Frey, B., Mayer, J., Mader, P., & Widmer, F. (2015). Distinct soil microbial diversity under long-term organic and conventional farming. *The ISME Journal*, 9, 1177–1194. <https://doi.org/10.1038/ismej.2014.210>
- Hawkesworth, S., & García Pérez, J. D. (2003). Potentials and constraints of the farmer to farmer programme for environmental protection in Nicaragua. *Land Degradation & Development*, 14, 175–188. <https://doi.org/10.1002/ldr.546>
- Hazen, R. M., & Sholl, D. S. (2003). Chiral selection on inorganic crystalline surfaces. *Nature Materials*, 2, 367–374. <https://doi.org/10.1038/nmat879>
- Jenks, W. S., Matsunaga, N., & Gordon, M. (1996). Effects of conjugation and aromaticity on the sulfoxide bond. *The Journal of Organic Chemistry*, 61, 1275–1283. <https://doi.org/10.1021/jo951504w>
- Khan, S. J. (2014). Biologically mediated chiral inversion of emerging contaminants. In D. A. Lambropoulou, & L. M. L. Nollet (Eds.), *Transformation products of emerging contaminants in the environment: Analysis, processes, occurrence, effects and risks* (pp. 261–279). Chichester, United Kingdom, UK: John Wiley and Sons Ltd.
- Lao, W., & Gan, J. (2012). Enantioselective degradation of warfarin in soils. *Chirality*, 24, 54–59. <https://doi.org/10.1002/chir.21023>
- Liu, W., Gan, J., Schlenk, D., & Jury, W. (2005). Enantioselectivity in environmental safety of current chiral insecticides. *Proceedings of the National Academy of Sciences*, 102, 701–706. <https://doi.org/10.1073/pnas.0408847102>
- Liu, X. G., Dong, F. S., Xu, J., Yuan, S. K., & Zheng, Y. Q. (2014). Dissipation and adsorption behavior of the insecticide ethiprole on various cultivated soils in China. *Journal of Integrative Agriculture*, 13, 2471–2478. [https://doi.org/10.1016/S2095-3119\(13\)60685-1](https://doi.org/10.1016/S2095-3119(13)60685-1)
- Magoč, T., & Salzberg, S. L. (2011). FLASH: Fast length adjustment of short reads to improve genome assemblies. *Bioinformatics*, 27, 2957–2963. <https://doi.org/10.1093/bioinformatics/btr507>
- Maia, A. S., Ribeiro, A. R., Castro, P. M. L., & Tiritan, M. E. (2017). Chiral analysis of pesticides and drugs of environmental concern: Biodegradation and enantiomeric fraction. *Symmetry*, 9. <https://doi.org/10.3390/sym9090196>
- Marom, H., Biedermann, P. U., & Agranat, I. (2007). Pyramidal inversion mechanism of simple chiral and achiral sulfoxides: A theoretical study. *Chirality*, 19, 559–569. <https://doi.org/10.1002/chir.20417>
- Masbou, J., Meite, F., Guyot, B., & Imfeld, G. (2018). Enantiomer-specific stable carbon isotope analysis (ESIA) to evaluate degradation of the chiral fungicide Metalaxyl in soils. *Journal of Hazardous Materials*, 353, 99–107. <https://doi.org/10.1016/j.jhazmat.2018.03.047>
- Moffat, A. S. (1993). New chemicals seek to outwit insect pests. *Science*, 261, 550–551. <https://doi.org/10.1126/science.8393587>
- Mueller, M. D., & Buser, H. R. (1995). Environmental behavior of acetamide pesticide stereoisomers. 2. Stereo- and enantioselective degradation in sewage sludge and soil. *Environmental Science & Technology*, 29, 2031–2037. <https://doi.org/10.1021/es00008a023>
- Pimentel, D. (1995). Amounts of pesticides reaching target pests: Environmental impacts and ethics. *Journal of Agricultural and Environmental Ethics*, 8, 17–29. <https://doi.org/10.1007/BF02286399>
- Poiger, T., Müller, M. D., Buser, H.-R., & Buerge, I. J. (2015). Environmental behavior of the chiral herbicide haloxyfop. 1. Rapid and preferential interconversion of the enantiomers in soil. *Journal of Agricultural and Food Chemistry*, 63, 2583–2590. <https://doi.org/10.1021/jf505241t>
- Potter, T. L., & Coffin, A. W. (2017). Assessing pesticide wet deposition risk within a small agricultural watershed in the Southeastern Coastal Plain (USA). *Science of the Total Environment*, 580, 158–167. <https://doi.org/10.1016/j.scitotenv.2016.11.020>
- Qi, Y., Liu, D., Luo, M., Jing, X., Wang, P., & Zhou, Z. (2016). Enantioselective degradation and chiral stability of the herbicide fluzifop-butyl in soil and water. *Chemosphere*, 146, 315–322. <https://doi.org/10.1016/j.chemosphere.2015.12.040>
- Qian, H., Lu, H., Ding, H., Lavoie, M., Li, Y., Liu, W. P., & Fu, Z. W. (2015). Analyzing Arabidopsis thaliana root proteome provides insights into the molecular bases of enantioselective imazethapyr toxicity. *Scientific Reports*, 5, 11975. <https://doi.org/10.1038/srep11975>
- Rey, S. L., Martínez, C. E., Merino, A. V., Vega, J. A., Fonturbel, M. T., & Simal, G. J. (2017). Polycyclic aromatic hydrocarbons in soil organic horizons depending on the soil burn severity and type of ecosystem. *Land Degradation & Development*, 29, 2112–2123. <https://doi.org/10.1002/ldr.2806>
- Sanganyado, E., Lu, Z., Fu, Q., Schlenk, D., & Gan, J. (2017). Chiral pharmaceuticals: A review on their environmental occurrence and fate processes. *Water Research*, 124, 527–542. <https://doi.org/10.1016/j.watres.2017.08.003>
- Schloss, P. D., Westcott, S. L., Ryabin, T., Hall, J. R., Hartmann, M., Hollister, E. B., ... Weber, C. F. (2009). Introducing mothur: Open-source, platform-independent, community-supported software for describing and comparing microbial communities. *Applied and Environmental Microbiology*, 75, 7537–7541. <https://doi.org/10.1128/AEM.01541-09>
- Shannon, P., Markiel, A., Ozier, O., Baliga, N. S., Wang, J. T., Ramage, D., ... Ideker, T. (2003). Cytoscape: A software environment for integrated models of biomolecular interaction networks. *Genome Research*, 13, 2498–2504. <https://doi.org/10.1101/gr.1239303>
- Siddig, A. H., Ellison, A. M., Ochs, A., Villar, L. C., & Lau, M. K. (2016). How do ecologists select and use indicator species to monitor ecological change? Insights from 14 years of publication in ecological indicators. *Ecological Indicators*, 60, 223–230. <https://doi.org/10.1016/j.ecolind.2015.06.036>
- Stegen, J. C., Lin, X., Konopka, A. E., & Fredrickson, J. K. (2012). Stochastic and deterministic assembly processes in subsurface microbial communities. *ISME Journal*, 6, 1653–1664. <https://doi.org/10.1038/ismej.2012.22>
- Sun, M., Liu, D., Zhou, G., Li, J., Qiu, X., Zhou, Z., & Wang, P. (2012). Enantioselective degradation and chiral stability of malathion in environmental samples. *Journal of Agricultural and Food Chemistry*, 60, 372–379. <https://doi.org/10.1021/jf203767d>
- Sun, R., Dsouza, M., Gilbert, J. A., Guo, X., Wang, D., Guo, Z., & Chu, H. (2016). Fungal community composition in soils subjected to long-term chemical fertilization is most influenced by the type of organic matter. *Environmental Microbiology*, 18, 5137–5150.
- Wang, Q., Garrity, G. M., Tiedje, J. M., & Cole, J. R. (2007). Naïve Bayesian classifier for rapid assignment of rRNA sequences into the new

- bacterial taxonomy. *Applied and Environmental Microbiology*, 73, 5261–5267. <https://doi.org/10.1128/AEM.00062-07>
- Wang, X., Li, Z., Zhang, H., Xu, J., Qi, P., Xu, H., ... Wang, X. (2013). Environmental behavior of the chiral organophosphorus insecticide acephate and its chiral metabolite methamidophos: Enantioselective transformation and degradation in soils. *Environmental Science & Technology*, 47, 9233–9240. <https://doi.org/10.1021/es401842f>
- Xiong, W., Li, R., Ren, Y., Liu, C., Zhao, Q., Wu, H., ... Shen, Q. (2017). Distinct roles for soil fungal and bacterial communities associated with the suppression of vanilla Fusarium wilt disease. *Soil Biology and Biochemistry*, 107, 198–207. <https://doi.org/10.1016/j.soilbio.2017.01.010>
- Yang, Z. H., & Ji, G. D. (2015). Stereoselective degradation and molecular ecological mechanism of chiral pesticides beta-cypermethrin in soils with different pH values. *Environmental Science and Technology*, 49, 14166–14175. <https://doi.org/10.1021/acs.est.5b04672>
- Ye, J., Zhao, M., Niu, L., & Liu, W. (2015). Enantioselective environmental toxicology of chiral pesticides. *Chemical Research in Toxicology*, 28, 325–338. <https://doi.org/10.1021/tx500481n>
- Zhang, K. K., Hu, D. Y., Zhu, H. J., Yang, J. C., & Song, B. A. (2014). Enantioselective degradation of dufulin in four types of soil. *Journal of Agricultural and Food Chemistry*, 62, 1771–1776. <https://doi.org/10.1021/jf404130d>
- Zhang, P., Yu, Q., He, Y., Zhu, W., Zhou, Z., & He, L. (2017). Chiral pyrethroid insecticide fenprothrin and its metabolite: Enantiomeric separation and pharmacokinetic degradation in soils by reverse-phase high-performance liquid chromatography. *Analytical Methods*, 9, 4439–4446. <https://doi.org/10.1039/c7ay01124e>
- Zhang, Q., Shi, H., Gao, B., Tian, M., Hua, X., & Wang, M. (2016). Enantioselective separation and determination of the chiral phenylpyrazole insecticide ethiprole in agricultural and environmental samples and its enantioselective degradation in soil. *Science of the Total Environment*, 542, 845–853. <https://doi.org/10.1016/j.scitotenv.2015.10.132>
- Zhang, Q., Zhang, Z., Tang, B., Gao, B., Tian, M., Sanganyado, E., ... Wang, M. (2018). Mechanistic insights into stereospecific bioactivity and dissipation of chiral fungicide triticonazole in agricultural management. *Journal of Agricultural and Food Chemistry*. <https://doi.org/10.1021/acs.jafc.8b01771>
- Zhang, Z., Gao, B., Li, L., Zhang, Q., Xia, W., & Wang, M. (2018). Enantioselective degradation and transformation of the chiral fungicide prothioconazole and its chiral metabolite in soils. *Science of the Total Environment*, 634, 875–883. <https://doi.org/10.1016/j.scitotenv.2018.03.375>
- Zhao, J., Luo, Q., Deng, H., & Yan, Y. (2008). Opportunities and challenges of sustainable agricultural development in China. *Philosophical Transactions of the Royal Society, B: Biological Sciences*, 363, 893–904. <https://doi.org/10.1098/rstb.2007.2190>
- Zhao, S., Li, K., Zhou, W., Qiu, S., Huang, S., & He, P. (2016). Changes in soil microbial community, enzyme activities and organic matter fractions under long-term straw return in north-central China. *Agriculture, Ecosystems and Environment*, 216, 82–88. <https://doi.org/10.1016/j.agee.2015.09.028>
- Zhou, J., Liu, W., Deng, Y., Jiang, Y.-H., Xue, K., He, Z., ... Wang, A. (2013). Stochastic assembly leads to alternative communities with distinct functions in a bioreactor microbial community. *MBio*, 4, 574. <https://doi.org/10.1128/mBio.00584-12>

## SUPPORTING INFORMATION

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