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ORIGINAL ARTICLE

# The fate and behavior of glufosinate-enantiomers and their metabolites in open-field soil and weeds

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Weed;
Soil

**Abstract** In this study, a chiral method based on high performance liquid chromatography–Q-Exactive Orbitrap Mass Spectrometry was developed to determine glufosinate stereoisomers and three metabolites in weed. Fortified recoveries in weed and soil samples were from 78.6 to 94.3 %, with relative standard deviations of less than 9.8 % and fortified values ranging from 0.04 to 40 mg/kg for the glufosinate enantiomers and 0.08–8 mg/kg for three metabolites. When glufosinate was given at the peak of weed growth in three orchards, it was mostly distributed and degraded in the weeds, with little remaining in the soil. The two glufosinate enantiomers degraded rapidly in the weeds and soils, with half-lives ranging from 0.7 to 3.1 days. The degradation of glufosinate enantiomers in Guizhou and Hunan weeds was enantioselective, with L-glufosinate being preferentially degraded. In Hainan weed, the degradation rate of the two enantiomers was nearly the same. In open field soils, glufosinate enantiomers were almost non-enantioselective. 3-methylphosphinico-propionic acid (MPP) was the primary glufosinate metabolite in weeds and soils, accounting for up to 14 % of the parent. *N*-acetyl-glufosinate (NAG) was relatively low, with less than 1 % of the parent glufosinate metabolized into 2-methylphosphinico-acetic acid (MPA).



## 1. Introduction

Enantiomers of chiral pesticides have similar physical and chemical properties, but the processes of chiral pollutant absorption, transformation, and degradation in the environment are enantioselective, leading to enantioselectivity in biological activity, toxicity, and environmental behavior (Ye et al., 2010; Zhao and Liu., 2011). Most chiral pesticides now produced are released into the environment as racemates, depending on separation, level of preparation, and cost. Because chiral analysis cannot identify enantiomers, evaluating the behavior of chiral pesticides in organisms or the environment only on racemate data is insufficient in the case of stereoselective behaviors.

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Therefore, it is critical to investigate the stereoselectivity of a chiral pesticide in plants and the environment to accurately assess food safety and environmental risk (Liu et al., 2008).

Glufosinate, D, L-2-amino-4-[hydroxy (methyl) phosphinoyl] butyric acid (Fig. 1), discovered by Hurst in the 1980 s, is widely used around the world to inhibit the growth of weeds and undesired plants (Lea., 1984). The herbicidal effect of glufosinate-ammonium is mediated by glutamine synthetase inhibition. Consequently, plants die in response to ammonia increase. This herbicide's action is mostly attributed to L-glufosinate (Hoerlein., 1994). Because of their polar structure, glufosinate stereoisomers and metabolites (Fig. 1) are readily soluble in water. The analytes' high boiling points make them difficult to identify directly using gas chromatography. Also, because of the lack of UV and fluorescent groups in glufosinate and its metabolites, direct detection by liquid chromatography (LC) is not possible. To analyze glufosinate in the environment and food samples, glufosinate is primarily derivatized using a derivatization reagent and then detected using LC, LC/MS, GC, e.t.c. (Hogendoorn et al., 1999; Royer et al., 2000; Oulkar et al., 2017; Li et al., 2015). Glufosinate, for example, was derivatized by 9-fluorenyl chloroformate and determined using LC-FLD (Oulkar et al., 2017). Royer et al. (2000) reported that glufosinate was derivatized with trifluoroacetic anhydride and subsequently identified by GC–MS/MS, as well as MPP and MPA. A few approaches for determining glufosinate by LC-MS/MS have been published by introducing sensitive MS detection technology (Nagatomi et al., 2013; Guo et al., 2018). However, because these studies used achiral methodologies, the enantiomers of glufosinate could not be distinguished.

The enantioselective ecological fate of chiral insecticides in the environment has gained increasing interest. It is critical to developing an analytical approach for studying chirality in environmental or biological samples to research the ecological fate of glufosinate stereoisomers. Hirose (2002) used precolumn derivatization with (+)-1-(9-fluorenyl) ethyl chloroformate to investigate the glufosinate enantiomers for the first time. Wang and Zhang (2015) separated the glufosinate enantiomers by HPLC-DAD using the chiral crown ether column CROWNPAK CR (+) (s-16-crown-6 ether coated on silica gel). Under laboratory conditions, we optimized the separation conditions on the stationary phase of the chiral crown ether and established the chiral analysis method to determine the degradation of two stereoisomers of racemic glufosinate in soil and water (Jia et al., 2019). According to Monika et al. (2002), the enantiomeric form of glufosinate used influenced the degradation of glufosinate in oilseed rape and corn cells, and D-glufosinate was stable in the plant cell. However, few studies have focused on the stereoselective environmental behaviours of glufosinate in plants (especially in weeds) and soil under open field condition.

According to information provided by China's Ministry of Agriculture, over 400 glufosinate-containing products have been registered for use in China; only three of these contain pure L-glufosinate. Therefore, most of the glufosinate released into the plant and the environment as racemates following treatment contains a pair of D-glufosinate and L-glufosinate. People always paid more attention to glufosinate's weed control effect and residue level on crops than to its degradation behaviour on target weeds. However, many weeds are also processed into feed, and pesticide residues in feed are critical to the safety of food consumed by livestock and human. The research then focuses on the following: (1) the development of an analytical method for the simultaneous determination of glufosinate enantiomers and their three metabolites without derivatization, (2) the investigation of glufosinate's possible stereoselective behavior in weeds and soil under open-field conditions, and (3) the formation trend of three glufosinate metabolites. The findings of this study will serve as the foundation for the environmental risk assessment of the chiral pesticide glufosinate.

## 2. Materials and methods

### 2.1. Chemicals and materials

The glufosinate-ammonium racemate standard (97.5 %) was obtained from Dr. Ehrenstorfer GmbH; the L-glufosinate standard (95.0 %) was obtained from the Shandong Institute of Pesticide; sodium *N*-acetyl glufosinate (95.0 %) was obtained from Toronto Research Chemicals; MPP (99.7 %) was obtained from Wako Pure Chemical Industry Co., ltd; MPA (99.0 %) was obtained from T (Nanjing, China). BASF SE (Germany) provided the 18 % commercial glufosinate soluble agent, while Thermo Fisher Scientific provided the LC-grade formic acid (Waltham, MA, USA). All additional chemicals

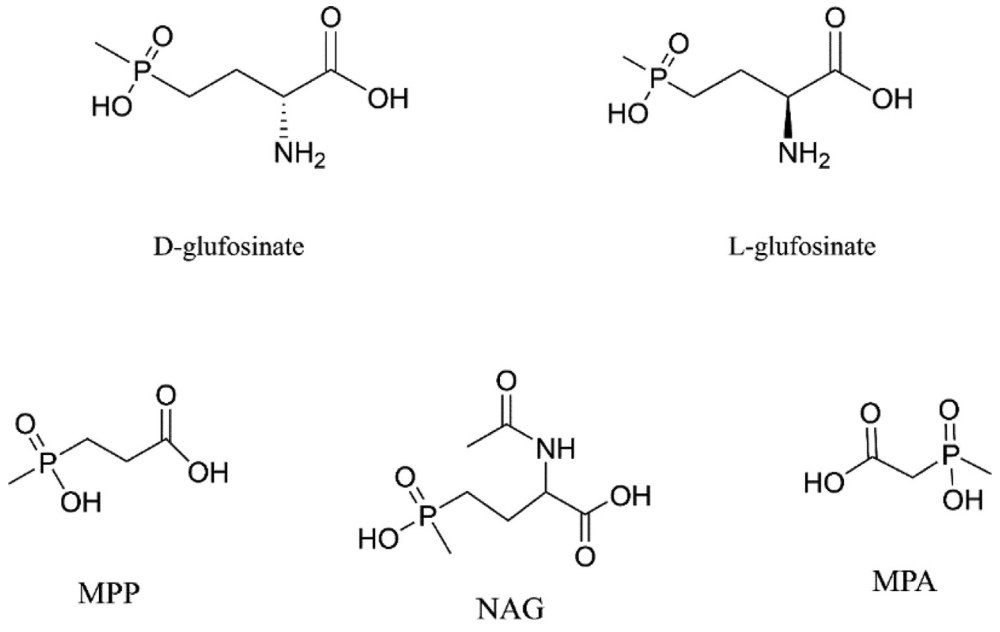


**Fig. 1** Chemical structure of D-glufosinate, L-glufosinate, MPP, NAG, and MPA.

and solvents are of analytical grade and were purchased from Jinshan Chemical Reagent Co. (Chengdu, China). The Watson Group provided distilled water (Hong Kong, China).

### 2.2. The preparation of standard solutions

In pure water, standard stock solutions of *rac*-glufosinate (398 μg/mL, D-glufosinate: L-glufosinate = 1:1), MPP (243 μg/mL), NAG (192 μg/mL), and MPA (209 μg/mL) were prepared. As mixed standard solutions, glufosinate, MPP, NAG, and MPA standard solutions were prepared in distilled water. For each analyte, standard mixed solutions were prepared and serially diluted with water to 0.005, 0.01, 0.05, 0.1, 0.5, 1, and 5 μg/mL. All solutions were stored in the dark at 4 °C. The matrix-matched standards ranged from 0.005 to 5 μg/mL for D-glufosinate and L-glufosinate, and from 0.01 to 1 μg/mL for MPP, NAG, and MPA, and were obtained by evaporating 1 mL of each solvent standard concentration at 55 °C and then dissolving in 1 mL blank extract.

### 2.3. Field trial

Based on the approved glufosinate application for citrus and banana orchards (dosage 540–810 g active ingredient per hectare (g a.i./ha), a field trial was conducted in Guiyang City, Guizhou Province, Changsha City, Hunan Province, and Haikou City, Hainan Province from May to July in 2019. A plot with no history of glufosinate use was chosen. To investigate the stereoselective degradation of glufosinate in weeds, the formulation was sprayed once at the indicated rate of 810 g a.i./ha during the peak of weed growth in the orchard. For this experiment, four test plots with lush weeds were prepared, three of which were used as replicas and the fourth as a control. Weed and soil samples were collected at random 2 h, 8 h, 1, 3, 5, 7, and 10 days following the application. The weed samples were cut into small pieces, selected using the quartering method, and stored at 20 °C until further analysis.

The soil samples were thoroughly mixed before being quartered and stored at 20 °C.

Simultaneously, four more plots were prepared without seed for the evaluation of stereoselective glufosinate degradation in open field soil. At the bare soil surface, the formulation was required at a rate of 810 g a.i./ha. Soil samples were collected from depths ranging from 0 to 10 cm at 15 randomly selected points 2 h, 8 h, 1, 3, 5, 7 and 10 days following application. The soil samples were thoroughly mixed before being quartered and stored at 20 °C.

*Conyza canadensis* (Linn.) *Cronq, Paspalum paspaloides* (Michx.) Scribn, and *Cynodon dactylon* (L.) Pers. were the most common weeds found in Guizhou citrus orchards. *Digitaria sanguinalis* (L.) Scop and *Eleusine indica* (L.) Gaertn were among the weeds found in a citrus orchard in Hunan. *Eleusine indica* (L) *Gaertner* and *Digitaria microbachne* (Presl) Henr were among the weeds found in Hainan banana orchards. Figures S1, S2, and S3 in the Supporting Information show photographs of the weeds in the field. Table 1 lists the physicochemical characteristics of the soils investigated.

### 2.4. Extraction of soil and weed samples

Weed or soil samples (5 g) in a 50-mL centrifuge tube were extracted for 30 min with 20 mL of distilled water by shaking. The organic matter was completely removed when 10 mL of dichloromethane was added, vortexed for 3 min, and the extract was centrifuged at 6000 rpm for 3 min. After transferring the extract to a new clean and dry centrifuge tube, 20 mL of purified water was added to the weed (or soil) sample. The extracts were combined after repeated extraction and purification. Before analysis, the 1.0 mL solution was filtered through a 0.22 μm nylon syringe filter and transferred to an autosampler vial.

### 2.5. Instrument settings for the analysis of D/L-glufosinate, MPA, MPP, and NAG

HPLC-HRMS (Q-Exactive Orbitrap, Thermo Fisher Scientific, Waltham, USA) with a CROWNPAK CR (+) chiral column (150 mm × 4.6 mm, 5 μm; Daicel, Japan) was used to evaluate glufosinate and its metabolites. The HPLC-HRMS determination conditions refer to the method developed earlier in this study group (Jia et al., 2019), and the specific conditions and parameters are presented in Table S1 (supporting information). In this method, the parent ions ($M + H^+$) with the exact ion mass (182.05767,139.01547, 153.03112, and 224.06824 $m/z$ for glufosinate, MPA, MPP, and NAG, respectively) were selected for quantitative analysis. The tolerance deviation of accuracy was set as 5 ppm, showing excellent specificity from the signals of matrix interferences.

### 2.6. Method validation

For method validation, the main parameters, such as linearity, accuracy, precision, the limit of quantification (LOQ), the limit

**Table 1** Physicochemical characteristics of the tested soils.

| Site | Particle size | | | pH[a] | Organic carbon[b] | CEC[c] |
|---|---|---|---|---|---|---|
| | Sand (%) | Silt (%) | Clay (%) | | | |
| Hunan | 43.20 | 38.24 | 18.56 | 4.93 | 3.87 | 18.32 |
| Guizhou | 33.16 | 37.00 | 29.84 | 5.33 | 5.10 | 23.51 |
| Hainan | 45.38 | 35.41 | 14.67 | 4.57 | 2.86 | 15.49 |

[a] Suspension of soil in water, 1:2.5 (w/w).
[b] Following the potassium dichromate volumetric method.
[c] Cation exchange capacity, following the ammonium acetate exchange method.

of detection (LOD) and matrix effect (ME), were studied according to the document SANTE/12682/2019 [SANTE, EC, 2019]. The linearity of both solvent and matrix-matched calibration curves were verified at five concentrations ranging from 0.005 to 5 μg/mL for D-glufosinate and L-glufosinate, and 0.01 to 1 μg/mL for MPP, NAG, and MPA, respectively. The ME was calculated using the slope ratio of the matrix-matched calibration curve versus the pure water calibration curve. If ME = 1, then no matrix effect is present. If ME > 1.5 or ME (%) less than 0.5, a strong matrix effect is present. If ME = 1.5 or 0.5, then a medium matrix effect is present. If 0.5 < ME > 1.5, then a weak mechanism effect is present (Gosetti et al., 2010).

Recovery studies were used to assess the accuracy and precision of this method, which was expressed as RSD at each fortified level. At various fortified concentrations, the recoveries of glufosinate enantiomers and their metabolites in weeds and soil were calculated (0.04, 0.4, 4, 40 mg/kg for D-glufosinate and L-glufosinate, 0.08, 0.8, 8 mg/kg for MPP, NAG, and MPA).

LOD was calculated using a signal-to-noise ratio of 3:1, while LOQ values were defined as the analytes' lowest spiking levels with acceptable recovery and precision.

### 2.7. Data analysis

The dissipation of glufosinate enantiomers in weeds and soil was investigated by plotting the concentration of their residues as a function of time. Regression analysis was used to obtain the analyte's corresponding rate constant k using a first-order kinetic equation (Equation (1)). Equation (2) was used to calculate the half-life ($t_{1/2}$, day).

$$Ct = C0e - kt \quad (1)$$

$$t1/2 = \ln 2/k \approx 0.693/k \quad (2)$$

Where $C_t$ and $C_0$ are the residues of D-glufosinate and L-glufosinate at time points (day) t and 0 (initial residues), respectively. And k is the dissipation rate constant.

The value of the enantiomeric fraction (EF) was used for the measurement of the stereoselective degradation of glufosinate in weeds and soil. EF values for glufosinate were defined by Equation (3).

$$EF = [D]/([D] + [L]) \quad (3)$$

Where [D] is the residues of D-glufosinate, [L] is the residues of L-glufosinate. The EF reveals whether the D-glufosinate content of the sample is more or less than its L-glufosinate content. The EF values range from 0 to 1, and the EF value for the racemic mixture was 0.5.

## 3. Results and discussing

### 3.1. Extraction and purification

Previous investigations used water, ammoniacal water, or acid water to extract glufosinate from various types of samples (Oulkar et al., 2017; Li et al., 2015; Jia et al., 2019; Pinto et al., 2018), and they found that water provided satisfactory recoveries. In this study, the recoveries of Glufosinate, MPA, MPP and NAG were significantly affected by extraction times. When extracted in one run using 20 mL of distilled water, the average recoveries of five target compounds in soils were 50.8 %–59.8 %, and the average recoveries in weeds were 47.7 %–78.0 %. When the soils were extracted twice, the recoveries of five target compounds in the soils reached 76.2 %–85.4 % at the same level (4 mg/kg). When the weeds were extracted twice, the recoveries of five target compounds in the weeds at the same level (4 mg/kg) reached 74.9 %–95.4 %.

To investigate the effect of the extraction solvent volume on extraction efficiency, two volumes of extract solvent (10 + 10 and 20 + 20 mL) were investigated in weed and soil. The recoveries of the five target analytes spiked in weed were in the ranges of 51.9 %–87.2 % and 72.5 %–107.5 % when the volumes of the water were 10 + 10 and 20 + 20 mL, respectively. The recoveries of the five target analytes spiked in soil were 42.4 %–97.3 % and 73.4 %–89.5 % when the volumes of the water were 10 + 10 and 20 + 20 mL, respectively. Therefore, 20 mL + 20 mL was selected as the extraction volume of the five target compounds. Next, three volumes of dichloromethane (10 + 10, 20 + 20 and 30 + 30 mL) were investigated in weed and soil. The recoveries of the five target analytes spiked in weed were in the ranges of 80.8 %–90.6 %, 82.9 %–91.2 % and 74.8 %-108.1 % when the volumes of the dichloromethane were 10 + 10, 20 + 20 and 30 + 30 mL, respectively. The recoveries of the five target analytes spiked in soil were in the ranges of 73.1 %–89.6 %, 79.2 %–102.8 % and 70.5 %–86.6 % when the volumes of the dichloromethane were 10 + 10, 20 + 20 and 30 + 30 mL, respectively. The recoveries were almost equal when different volumes of dichloromethane were used. To save reagents, 10 + 10 mL of dichloromethane was selected as the purifying agent for liquid–liquid extraction. (See Fig. 2).

(A: Volume of extract solvent in weed; B: Volume of $CH_2Cl_2$ in weed; C: Volume of extract solvent in soil; D: Volume of $CH_2Cl_2$ in soil).

### 3.2. Method validation

Table S2 summarizes the regression equations, matrix effect, LOQs, and LODs for each analyte (In Supporting Information). Both glufosinate and NAG are chiral compounds having distinct enantiomers. However, because the proposed chiral method was developed exclusively for determining glufosinate stereoisomers, the NAG enantiomers were not differentiated in this study; instead, the latter was considered as a single substance. In weeds and soil, good linearities (R2 > 0.993) were observed for D-glufosinate, L-glufosinate, MPP, NAG, and MPA. Matrix effects, such as matrix enhancement or suppression, are common issues in HPLC-MS, influencing the method's reproducibility and accuracy (Gosetti et al., 2010). The ME values of five target compounds in extracts of weeds and soils from three separate orchards ranged from 0.19 to 1.86. In three soil extracts with ME ranging from 0.50 to 1.03, for example, a moderate to no suppression of the signal for D-glufosinate and L-glufosinate was seen. However, the ME values of D-glufosinate and L-glufosinate in three weed extracts ranged from 0.29 to 1.32. To eliminate the matrix effect and provide more accurate results, each analyte was quantified using the relevant soil matrix or weed matrix standards. Table S3 shows the recoveries and RSDs of five analytes in quintuplicate at four different spiked levels (In Supporting

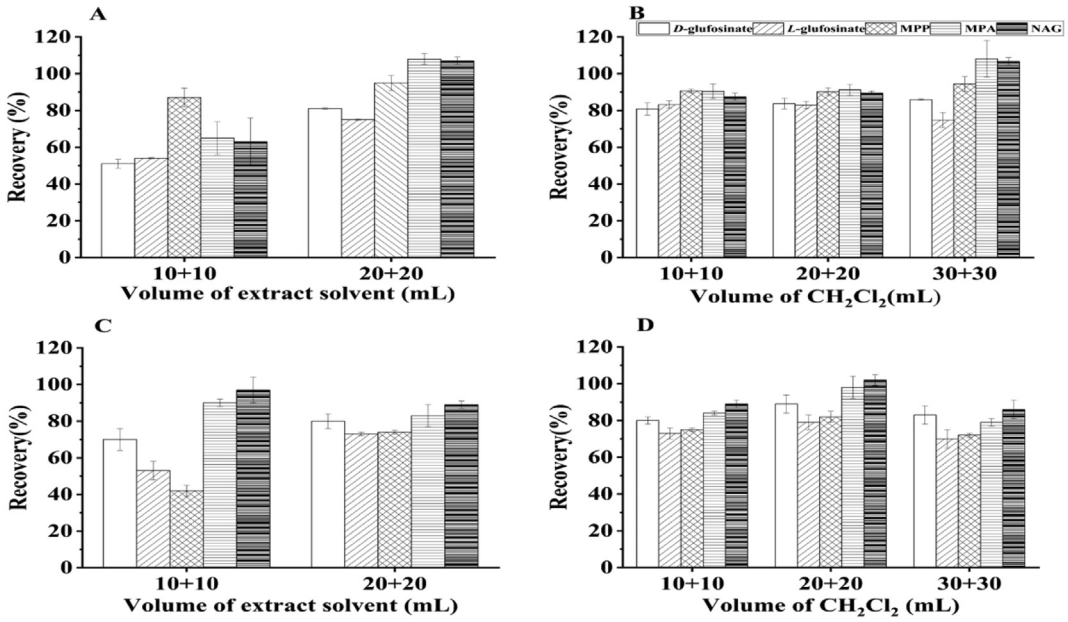


**Fig. 2** Recovery results under different extraction and purification volumes (spik level 4 mg/kg, n = 3).

Information). The ratio of D-glufosinate to L-glufosinate did not change during the experiment and always remained 1:1. This suggested method shows adequate average recoveries at spiked levels ranging from 0.04 to 40 mg/kg and from 78.6 to 94.3 %, as well as good precision with all RSD values less than 10 % for all five analytes in soil and weeds. The peak order of the two glufosinate enantiomers was confirmed using the L-glufosinate standard. Fig. 3 depicts typical glufosinate and its metabolite chromatograms.

A, standard solution (0.01 μg/mL), B, blank banana sample, C, matrix-matched standard solution (0.01 μg/mL), and D, soil spiked sample (0.08 mg/kg).

### *3.3. Stereoselective degradation of glufosinate in weed*

Fig. 4 shows glufosinate degradation in weeds. The two stereoisomers dissipated according to first-order kinetics in weeds from Guizhou, Hunan, and Hainan. This experiment employed a commercial racemate of glufosinate. However, the initial residue of L-glufosinate in Hunan weeds was 35.49 mg/kg, which was lower than D-glufosinate with 52.76 mg/kg, indicating that weeds rapidly degraded L-glufosinate with an EF value of 0.60 at 2 h after spraying (Fig. 4H). Other chiral pesticides have been reported to degrade preferentially after 2 h of spraying. For example, (-)-propiconazole degraded preferentially 2 h after spraying, exhibiting clear stereoselective degradation (Cheng et al., 2017). At the same time, after spraying, the EF values of glufosinate stereoisomers increased from 0.50 to 0.63 in Guizhou weeds, demonstrating that weeds preferentially degraded L-glufosinate (Fig. 4G). The EF values in Hainan weed stayed around 0.5 during the 0–3 d period (Fig. 4I), and the degradation rate reached 97 %. So, the degradation curves of the two enantiomers nearly coincided (Fig. 4C), and the half-lives of the two enantiomers were almost identical, even if EF values deviated from 0.5 at the later stages of degradation in Hainan.

(A-C) Dissipation curves of D-glufosinate and L-glufosinate in Guizhou, Hunan, and Hainan weeds, (D-F) Percentage of metabolites relative to the parent in weeds, (G-H) EF values versus time of glufosinate stereoisomers in weeds.

(*The heavy rainfall that occurred from days 6 to 10, so, the residual amounts of the target compounds recorded in samples collected from Guizhou on days 7 and 10 were lower than the LOQ, the time scale on the X axis was only 0–5 d).

The dissipation half-life and kinetic equations of D-glufosinate and L-glufosinate in weeds in Guizhou, Hunan, and Hainan are shown in Table 2. The curves corresponding to the first-order model are shown in Figures S4 in Supporting Information. D-glufosinate and L-glufosinate had half-lives of 1.3 and 0.7 days, respectively, in Guizhou weeds, 2.4 and 1.1 days in Hunan weeds, and 1.8 and 2.0 days in Hainan weeds. It demonstrated rapid glufosinate degradation in weeds. Other plants have also shown rapid glufosinate degradation. Chen discovered that glufosinate degraded rapidly in non-genetically modified rape leaves, with a dissipation rate of 50 % a day after application. The half-life of glufosinate in transgenic herbicide-resistant rape leaves is 5.3 days, while it is 3.0 days in non-genetically modified rape leaves (Chen et al., 2018).

Metabolites (MPP, NAG, and MPA) were discovered as well (Fig. 4). In different matrices, the percentage of the three metabolites compared to the parent was calculated. MPP residue in Guizhou weeds increased gradually from 0.40 to 1.57 mg/kg, reaching a maximum of 3.72 percent of the parent after three days. The initial NAG residue in the Guizhou weed was relatively low, reaching 0.34 mg/kg and a high of 0.46 % of the parent after three days (Fig. 4D). MPA levels in Guizhou were low throughout the investigation, culminating at 0.09 mg/kg. MPP and NAG levels in Hunan and Hainan weed, on the other hand, were greater than in Guizhou weed. On day 7, the MPP and NAG levels of Hunan weeds peaked at 14.19 and 5.39 % of the parent substance, respectively

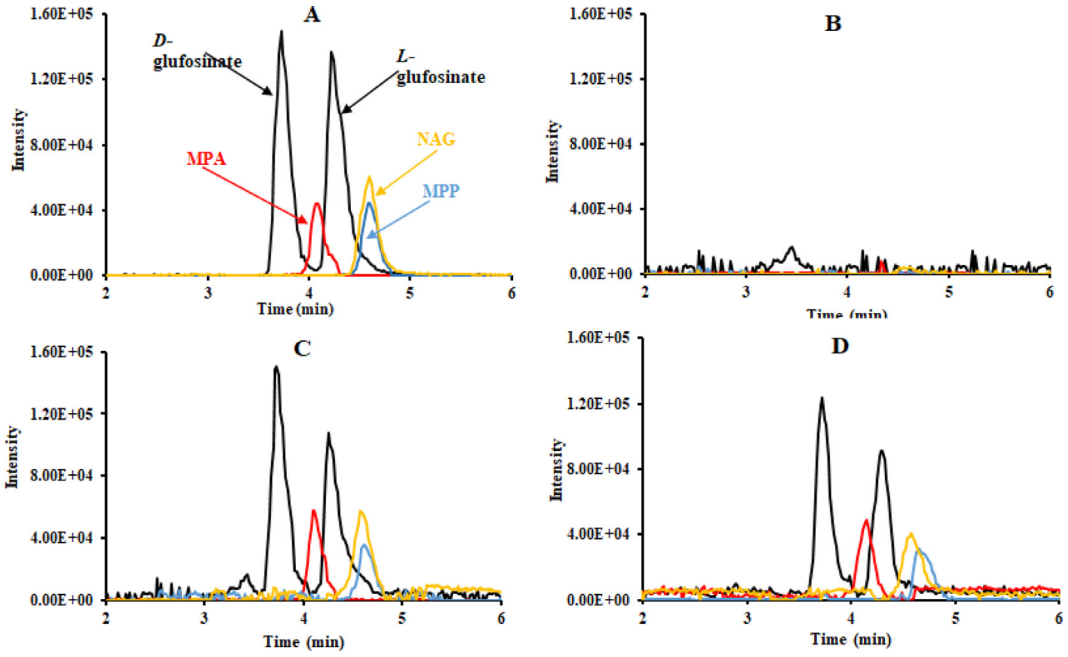


**Fig. 3** Typical LC-MS/MS glufosinate enantiomers and their metabolites in soil.

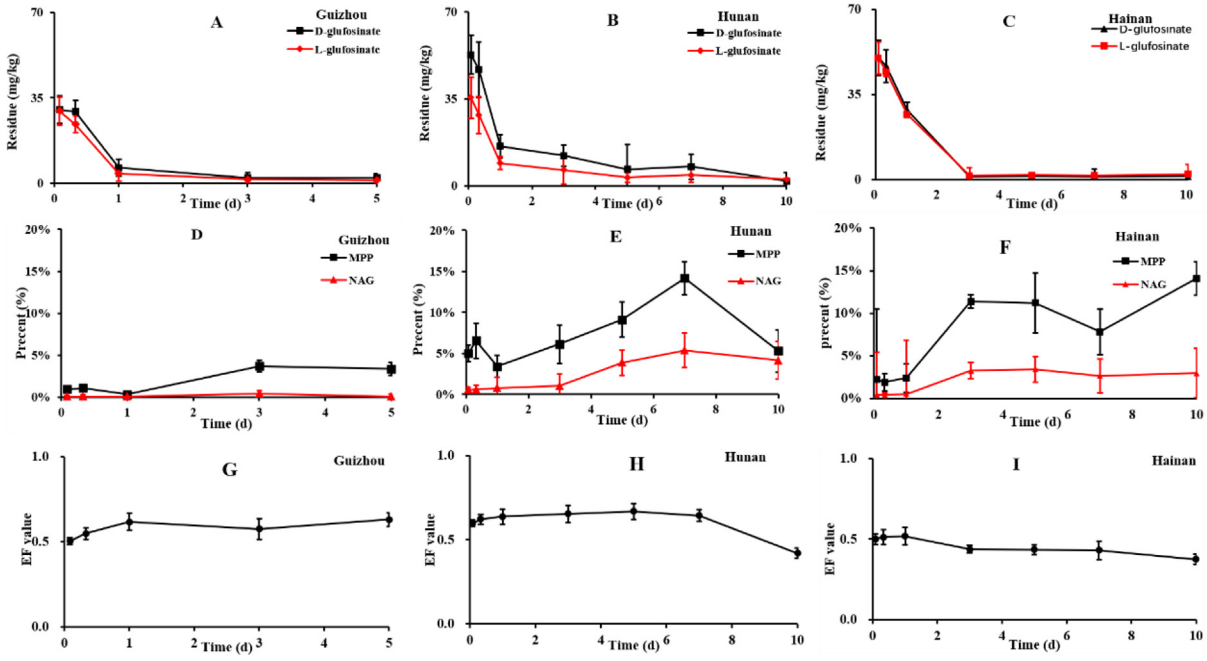


**Fig. 4** The degradation of glufosinate in weeds under field conditions (n = 3).

(Fig. 4E). MPP in Hainan weeds reached 14.08 % of the parent material on day 10, while NAG almost remained at 3 % of the parent material after day 3. (Fig. 4F). Monika et al. observed that the transformation rate of glufosinate in sensitive and transgenic rape cells is lower (3–10 %) than in rapeseed cells (20–43 %); also, the contents of metabolites in rape cells differed from those in corn cells. So, we hypothesize that the levels of MPP and NAG in Guizhou weeds are lower than in Hunan and Hainan weeds, most likely because of changes in the type of weed collected across the sampling locations. Figure S1-S3 depicts the various types of weeds found in two citrus farms and one banana orchard. The weeds in the three locations may include varying amounts and types of chemical compounds (e.g., enzymes and organic acids), which could alter glufosinate degradation. Throughout the experiment, MPP levels were consistently higher than NAG and MPA levels. MPP was the most abundant glufosinate metabolite in weeds from three locations, NAG was relatively low, and only a small amount of glufosinate (i.e. 1 % of the parent compound) was metabolized to MPA.

**Table 2** Dissipation kinetic equation and a half-life of D-glufosinate and L-glufosinate in weed.

| Matrix | Analyte | Dynamic equation | $R^2$ | Half-life (days) |
|---|---|---|---|---|
| Guizhou weed | D-glufosinate | $C = 22.03e^{-0.551t}$ | 0.7862 | 1.3 |
| | L-glufosinate | $C = 24.30e^{-0.973t}$ | 0.8436 | 0.7 |
| Hunan weed | D-glufosinate | $C = 37.36e^{-0.292t}$ | 0.8877 | 2.4 |
| | L-glufosinate | $C = 34.69e^{-0.636t}$ | 0.7335 | 1.1 |
| Hainan weed | D-glufosinate | $C = 26.283e^{-0.391t}$ | 0.9395 | 1.8 |
| | L-glufosinate | $C = 25.368e^{-0.346t}$ | 0.9184 | 2.0 |

### *3.4. Degradation of glufosinate enantiomers in soil*

The formulation was applied to the bare soil surface at a rate of 810 g a.i./ha, and the degradation of glufosinate in the open field soil was also investigated. D-glufosinate and L-glufosinate dissipation in two soils followed first-order kinetics (Fig. 5A, 5B, 5C). The curves corresponding to the first-order model are shown in Figures S5 in Supporting Information. Table 3 reveals that glufosinate degraded quickly in open field soil, with the half-life of D-glufosinate and L-glufosinate being 1.3, 1.1 days, and 1.6, 1.6 days in Guizhou and Hainan soil, respectively, and 3.1, 3.1 days in Hunan soil (Table 3). The EF value in Hunan soil (Fig. 5H) remained constant at 0.5 over time, showing that D-glufosinate and L-glufosinate were degraded at the same rate and half-lives. The EF values in Hainan soil stayed around 0.5 during the 0-5d period (Fig. 5I), with a degradation rate of 97. So, the half-lives of the two enantiomers were nearly identical, even when EF values deviated from 0.5 in the later stages of degradation. The situation in Guizhou was like that in Hainan, and the half-lives of the two enantiomers were nearly identical. Table 1 shows the physicochemical properties of the soils investigated. Overall, the data demonstrated that the two enantiomers degraded quickly and at nearly the same rate in the three orchard soils. The half-life of glufosinate in open-field soils has been observed to be between 1.4 and 4.3 days (Faber et al., 1997; Zhang et al., 2014; Jian et al., 2015). Glufosinate in the soil can be degraded and detoxified through oxidation, transamination, and *N*-acetylation, and the bacteria that degrade it are easily discovered (Bartsch and Tebbe., 1989; Hsiao et al.,2009).

(A-C) Dissipation curves of D-glufosinate and L-glufosinate in Guizhou, Hunan, and Hainan soils, (D-F) Percentage of metabolites relative to the parent in soils, (G-I) EF values versus time of glufosinate stereoisomers in soils.

On day 5, MPP in Guizhou soil peaked at 9.86 % of the parent. At 2 h after application, NAG in Guizhou soil reached a maximum of 2.14 % compared to the parent (Fig. 5C). On

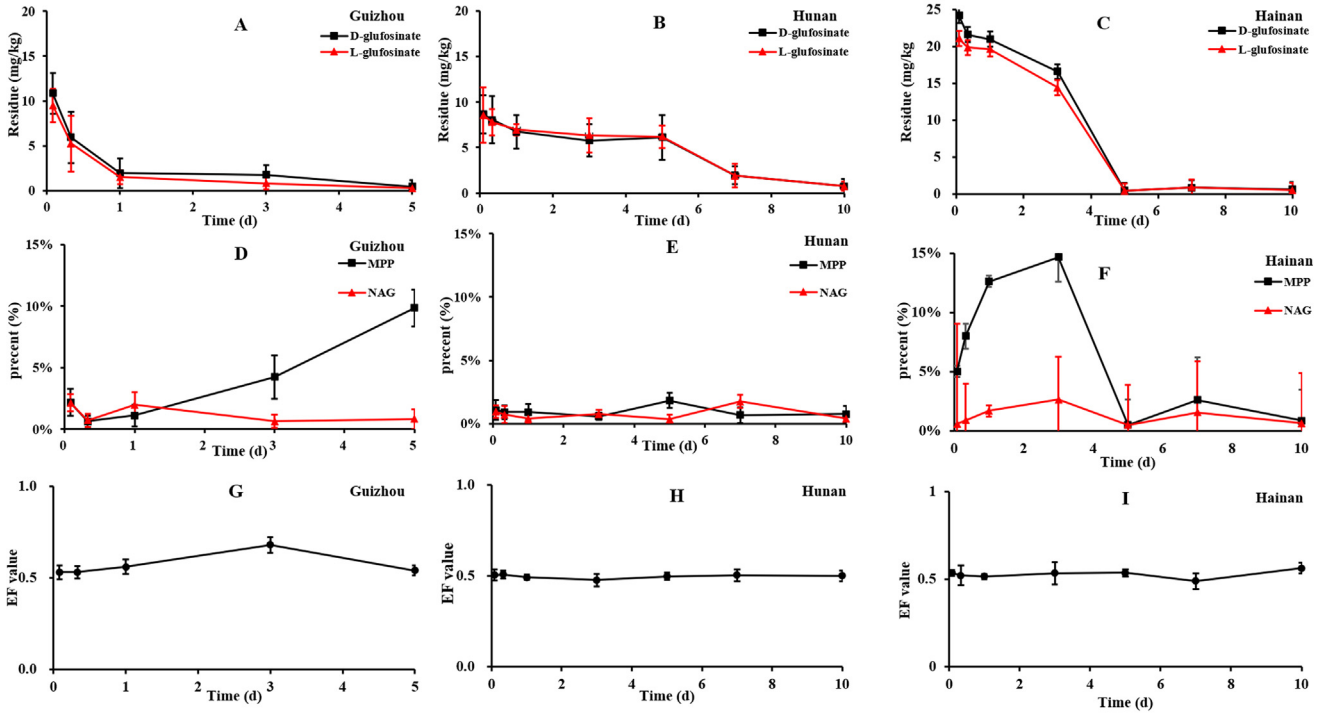


**Fig. 5** The degradation of glufosinate in soil under the field condition (n = 3).

**Table 3** Dissipation kinetic equation and a half-life of D-glufosinate and L-glufosinate in soil.

| Matrix | Analyte | Dynamic equation | $R^2$ | Half-life (days) |
|---|---|---|---|---|
| Guizhou soil | D-glufosinate | $C = 6.99e^{-0.538t}$ | 0.8568 | 1.3 |
| | L-glufosinate | $C = 5.99e^{-0.656t}$ | 0.9016 | 1.1 |
| Hunan soil | D-glufosinate | $C = 9.96e^{-0.227t}$ | 0.8792 | 3.1 |
| | L-glufosinate | $C = 10.09e^{-0.227t}$ | 0.8702 | 3.1 |
| Hainan soil | D-glufosinate | $C = 24.46e^{-0.434t}$ | 0.8582 | 1.6 |
| | L-glufosinate | $C = 24.6e^{-0.440t}$ | 0.8585 | 1.6 |

day 5, MPP in Hunan soil reached 1.82 percent relative to the parent, while NAG peaked at 1.74 % relative to the parent (Fig. 5D). On the third day, MPP and NAG in Hainan soils achieved a maximum of 14.7 and 3.0 percent relative to the parent, respectively. The MPP concentration of Hainan soils is higher than that of Guizhou and Hunan soils. In those conditions, less than1% of the glufosinate was converted to MPA.

### *3.5. Distribution of glufosinate in weeds and soil in the peak period of weeds growth*

To evaluate the distribution of glufosinate on the soil and weeds following the glufosinate application in the field, soils under the weeds were collected and analyzed 2 h after application. The experiment was conducted during the summer. Weeds grew well throughout this season and completely covered the earth; the soil beneath the weeds could not be seen (Figures S1, S2, and S3 in the Supporting Information). At 2 h, the total residues of glufosinate enantiomers were 0.07 mg/kg in Guizhou soil, 0.06 mg/kg in Hunan soil, and 0.02 mg/kg in Hainan soil. At 2 h, the total glufosinate residue levels in Guizhou, Hunan, and Hainan weeds were 59.71, 88.25, and 100.41 mg/kg, respectively. The total residual of two enantiomers of glufosinate in weed was 853, 1470, and 5020 times that in the soil in Guizhou, Hunan, and Hainan, respectively. Throughout the experiment, overall glufosinate residues in the soil remained low, and glufosinate enantiomer residues in the soil were practically below LOQ. This discovery indicates that glufosinate is mostly distributed and degraded in the weeds after application during the peak period of weed growth.

## 4. Conclusions

In this study, a rapid chiral method based on HPLC–HRMS (Q-Exactive Orbitrap) was developed to determine glufosinate enantiomers and three metabolites in weeds and soil at the same time. The findings revealed glufosinate was primarily distributed and degraded in weeds following application. Weeds degraded glufosinate quickly, and L-glufosinate was preferentially degraded after spraying in Guizhou and Hunan weeds. While L-glufosinate and D-glufosinate degraded nearly equally in Hainan weed. In three orchard soils under open field conditions, the two enantiomers degraded quickly and nearly at the same rate, with half-lives of less than 3.1 days. MPP was the primary glufosinate metabolite in weeds and soils, reaching a maximum of 14 % relative to the parent during the degradation stage, whether in weeds or soil. The metabolite NAG is also a chiral compound. NAG did not achieve the desired separation, and more extensive separation screening is required. Overall, this study provided valuable information for the environmental risk assessment of glufosinate on the enantiomeric level.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.arabjc.2022.104191.

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