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# Enantioselective degradation and chiral stability of the herbicide fluazifop-butyl in soil and water

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## HIGHLIGHTS

- The stereoselective degradation and transformation of fluazifop-butyl in soil and water were studied.
- The chiral stability of fluazifop-butyl enantiomers was investigated.
- The formation, degradation and enantioselectivity of the primary metabolite fluazifop were studied.
- Enantioselective degradations were found in Beijing and Anhui soil.
- There was no significant enantioselectivity of the degradation of fluazifop-butyl in water.

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## ABSTRACT

The stereoselective degradation and transformation of the enantiomers of the herbicide fluazifop-butyl in soil and water were studied to investigate the environmental behavior and chiral stability of the optical pure product. Its main chiral metabolite fluazifop was also monitored. LC/MS/MS with Chiralpak IC chiral column was used to separate the enantiomers of fluazifop-butyl and fluazifop. Validated enantioselective residue analysis methods were established with recoveries ranging from 77.1 to 115.4% and RSDs from 0.85 to 8.9% for the enantiomers. It was found the dissipation of fluazifop-butyl was rapid in the three studied soils (Beijing, Harbin and Anhui soil), and the degradation half-lives of the enantiomers ranged from 0.136 to 2.7 d. Enantioselective degradations were found in two soils. In Beijing soil, R-fluazifop-butyl was preferentially degraded leading to relative enrichment of S-enantiomer, but in Anhui soil, S-fluazifop-butyl dissipated faster. There was no conversion of the R-fluazifop-butyl into S-fluazifop-butyl or vice versa in the soils. The formation of fluazifop in the soils was rapidly accompanied with the fast degradation of fluazifop-butyl, and the enantioselectivity and the transformation of S-fluazifop to R-fluazifop were found. The degradation of fluazifop-butyl in water was also quick, with half-lives of the enantiomers ranging from 0.34 to 2.52 d, and there was no significant enantioselectivity of the degradation of fluazifop-butyl and the formation of fluazifop. The effects of pH on the degradation showed fluazifop-butyl enantiomers degraded faster in alkaline conditions. This study showed an evidence of enantioselective behavior and enantiomerization of the chiral herbicide fluazifop-butyl.



## 1. Introduction

Pesticides are widely used in agriculture where they have played very important roles, especially in crop yield. Recently, chiral pesticides have attracted more and more attention for the different bioactivity, toxicity and environmental behaviors of the enantiomers. More than 28% of commercial pesticides are chiral (Ulrich et al., 2012) for they have two or more enantiomers. The chirality derived from the chiral carbon, sulfur or phosphorus atoms in the chemical structures (Hegeman and Laane, 2001). The enantiomers of chiral pesticides have the same physical and chemical properties in achiral environment, but they often exhibit different toxicity, metabolism, biological activity and degradation behavior in chiral environment, sometimes even performed opposite physiological effects (Millership and Fitzpatrick, 1993; Maier et al., 2001; Liu and Gan, 2004).

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After being applied to the field, chiral pesticides may be affected by enzymes, microbes, organic matters and other chiral macromolecules. So the enantiomers of chiral pesticides can be eliminated selectively, or even isomerized. In recent years, many studies have focused on the selective behavior of chiral pesticides, and there are many factors affecting the enantioselective behavior of pesticides, such as pH, redox conditions, anaerobic/aerobic conditions etc. Chen (Chen and Liu, 2009) studied the degradation of Rac- and R-metalaxyl under anaerobic conditions and found that the preferential degradation of S-enantiomer, resulted in relative enrichment of the R-(−)- enantiomer. Diao et al. (2010a) investigated the degradation of lactofen and its main metabolites in sediment under laboratory conditions and the results showed S-(+)-lactofen and S-(+)-desethyl lactofen degraded much faster than the R-enantiomer. At present, most chiral pesticides are produced and used in the form of racemates. People have tried to develop optically pure products which contain only the active enantiomer(s) to increase the efficacy and decrease the contamination. Several single- or enriched enantiomer pesticide formulation have been developed and used (Liu et al., 2015b) such as metalaxyl-M (Zadra et al., 2002), S-metolachlor (Cao et al., 2008), quizalofop-p-ethyl (Mantzos et al., 2015), fluazifop-p-butyl (Fan et al., 2013) and fenoxaprop-p-ethyl (Chen et al., 2011). In an ideal world, chiral structures of the chiral pesticides should be stable and preferential degradation should not occur. But as mentioned above, chiral pesticide enantiomers can be influenced by many factors in the environment and the environmental behaviors cannot be anticipated. Racemization may be occurred after the application of optically pure pesticides. If the chiral structures cannot be maintained in the field, the development of optically pure chiral pesticides is of no significance. Therefore, it is necessary to study the enantioselective degradation and stability of chiral pesticide enantiomers in the environment.

Fluazifop-butyl, butyl (RS)-2-[4-(5-trifluoromethyl-2-pyridyloxy-) phenoxy-] propionate (Fig. 1), belongs to the aryloxyphenoxy-propionate (AOPP) herbicide family. Only R enantiomer is herbicidally active and it has been developed as optically pure herbicide and widely used (Kulshrestha et al., 1995). Fluazifop-P-butyl is already a commercial formulation of the enriched R-enantiomer and widely applied. However, the registration of fluazifop-butyl product is still effective in China. Fluazifop-butyl is used for postemergence control of graminaceous weeds in a range of broad-leaved crops (Negre et al., 1988). When applied, it degraded quickly to its major metabolite, the free acid, fluazifop 2-[4-(5-trifluoromethyl-2-pyridyloxy-)-phenoxy-] propionic acid, which is also chiral (Carr, 1986; Zanco et al., 1992). Fluazifop-butyl rapidly dissipated in the environment with half-lives in the range of 1.11–24.6 d (Kulshrestha et al., 1995; Fan et al., 2013) but fluazifop is relatively persistent. However, information on the change of an isomeric ratio for chiral pesticides in residue analysis and enantiomerization is very limited.

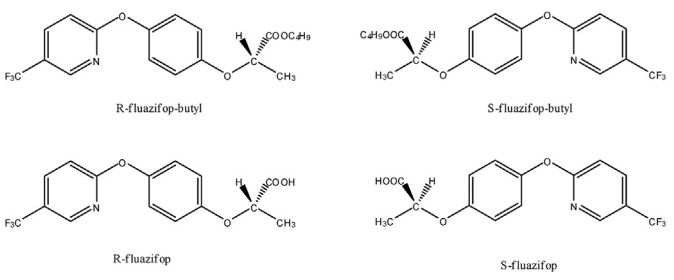


**Fig. 1.** Structures of fluazifop-butyl and fluazifop.

In this work, the enantiomers of fluazifop-butyl and its metabolite fluazifop were separated and a sensitive and effective residue analysis method for the enantiomers in soil and water samples were developed. Based on that, the enantioselective degradation of fluazifop-butyl and fluazifop in soil and water was studied and the impact of pH on the degradation was also investigated. The degradation of single enantiomers was conducted to confirm the chiral stability. This study emphasizes the importance of the fate of both enantiomers of chiral pesticide in an environmental system for the rational use of optically pure products. This work can provide evidence for chiral pesticide risk assessment and suggestions for optically pure pesticide development and application.

## 2. Materials and methods

### 2.1. Chemicals and materials

Fluazifop-butyl (90.4%) and R-fluazifop-butyl (95.0%) were provided by Institute for Control of Agrichemicals Ministry of Agriculture. S-fluazifop was prepared on cellulose-tri-(3, 5-dimethylphenylcarbamate)-based chiral column (CDMPC-CSP, provided by the Department of Applied Chemistry, China Agricultural University, Beijing). Fluazifop and R-fluazifop (purity > 90%) were synthesized in our laboratory. Water was prepared by Millipore purification system. Methanol (HPLC grade) was obtained from Merck (Darmstadt, Germany). All of the other chemicals and solvents were of analytical grade and purchased from commercial sources.

### 2.2. Instrument analysis

A Thermo Xcalibur™ LC/MS/MS system (Thermo Electron Corporation, Hopkinson, MA) was used for the separation of fluazifop-butyl and fluazifop enantiomers. The liquid chromatography (Thermo ACCELA series) was equipped with ACCELA Autosampler, ACCELA 600 pump, a 20 μL injection loop and a 2 μL flow cell. Mass spectrometry system was operated in the electrospray ionization (ESI) turbo ion source positive ion mode. Thermo Xcalibur 2.2 SP1.48 software was used for data management and control. The major optimized working parameters were as follows: Spray Voltage 3500 V, Vaporizer Temperature 200 °C, Sheath Gas Pressure 35 psi, Aux Gas Pressure 15 arbitrary units, Capillary Temperature 350 °C, Capillary Offset 35 V, Q2 Collision Gas Pressure 1.5 mTorr. Acquisition was performed in selected reaction monitoring (SRM) mode and the corresponding conditions were summarized in Table S1 (Supplementary material).

### 2.3. The separation of fluazifop-butyl and fluazifop enantiomers

Enantiomers were separated on a Chiralpak IC (250 × 4.6 mm I.D., 5-μm particles). For the separation of fluazifop enantiomers, the mobile phase was methanol/0.1% (v/v) aqueous formic acid (68/32, v/v). Methanol/0.1% (v/v) aqueous formic acid (80/20, v/v) was used to separate the enantiomers of fluazifop-butyl. The standard solution of fluazifop-butyl, R-fluazifop-butyl, fluazifop and R-fluazifop in methanol were detected, respectively. The first eluted enantiomers were R-fluazifop-butyl and R-fluazifop, respectively. (Fig. 2). The column temperature was maintained at 25 °C and the injection volume was 5 μL. The flow rate was 0.5 mL/min. The final concentration of each enantiomer was 0.025 mg $kg^{-1}$. The capacity factors ($k_1$ and $k_2$ for the first and second eluted enantiomers), separation factors ($\alpha$), and resolutions (Rs) were calculated. For fluazifop-butyl the parameters were: $k_1 = 6.81$, $k_2 = 8.45$, $\alpha = 1.24$, Rs = 1.57, and for fluazifop: $k_1 = 1.81$, $k_2 = 2.14$, $\alpha = 1.18$, Rs = 1.87.