

Enantioselective toxicity and degradation of chiral herbicide fenoxaprop-ethyl in earthworm *Eisenia fetida*



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ABSTRACT

The enantioselective degradation of fenoxaprop-ethyl in ecological indicator earthworm was studied and the main metabolites (fenoxaprop, 6-chloro-2,3-dihydrobenzoxazol-2-one, ethyl-2-(4-hydroxyphenoxy)propanoate, 2-(4-hydroxyphenoxy)propanoic acid) were also monitored on an enantiomeric level. The individual enantiomers of fenoxaprop-ethyl and its three chiral metabolites were prepared to study the acute toxicity to earthworm. Chiral analysis methods were set up based on HPLC–MS/MS with chiralpak IC chiral column. Fenoxaprop-ethyl was not found in earthworms, while the primary metabolite fenoxaprop was in relatively high levels indicating a quick hydrolysis degradation. Fenoxaprop was accumulated almost exclusively with R-enantiomer in earthworms and the bio-concentration factors of R-fenoxaprop and S-fenoxaprop were 1.39 and 0.17 respectively with the enantiomer fraction (EF) values about 0.99. The degradation of R-fenoxaprop in earthworms followed first-order kinetics with half-life of 1.82 day. The other metabolites could not be detected in earthworms. The calculated LC₅₀ values showed ecological indicator earthworm was more sensitive to the four metabolites than fenoxaprop-ethyl. Furthermore, earthworm was more sensitive to the R-form of the chiral metabolites than the S-form and rac-form. The results suggested metabolites and enantioselectivity should be taken into consideration to better predict the exposure concentration and apply ecological indicators in toxicological studies.

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1. Introduction

In 2009, almost 30 percent of the registered pesticides have stereogenic center and at least two mirror image enantiomers, and more than 40% of used pesticides in China were chiral (Qu et al., 2014; Ying et al., 2009). The physical and chemical properties of the enantiomers in non-chiral environment are identical. Despite of the differences in bioactivity, toxicity and metabolism, a majority of chiral pesticides have been produced and used as racemate (Cai et al., 2008; Liu et al., 2009). Only concerning the difference between the chiral enantiomers can the environmental risk assessment be credible.

Earthworm (*Eisenia fetida*) is an important soil organism which comprises the largest part of the soil fauna biomass and plays a significant role in soil ecology. Earthworm living in topsoil has a thin and permeable cuticle, which processes a large amount

of soil through their feeding and burrowing activities and acts as an early-warning system for emerging soil ecological environment deteriorating (Jager et al., 2005; Lavelle et al., 1997; Shan et al., 2010). Because earthworm can accumulate various contaminants (Šmídová and Hofman, 2014; Wen et al., 2015; Zhang et al., 2014), they are excellent indicators for evaluating the bioaccumulation potential of chemicals (Aly and Schröder, 2007; Armitage and Gobas, 2007). Some terrestrial vertebrate species like birds and small mammals are common predators of earthworm, therefore earthworm is important to the biomagnification of soil contamination. US Environmental Protection Agency (EPA), Ministry of Agriculture of China and Organization for Economic Cooperation and Development (OECD) had used earthworm (*Eisenia fetida*) as a model organism for assessing the potential biological effect of the chemicals released into the environment. In order to evaluate the impacts of pollutants on earthworms, mortality is most frequently checked. Furthermore, growth and reproductive parameters are also often invested.

Fenoxaprop-ethyl (FE, Fig. 1), (±)-ethyl 2-[4-[(6-chloro-2-benzoxazolyl)oxy]phenoxy]propanoate, as a kind of aryloxyphenoxypropionate herbicides, can inhibit acetyl-CoA carboxylase in

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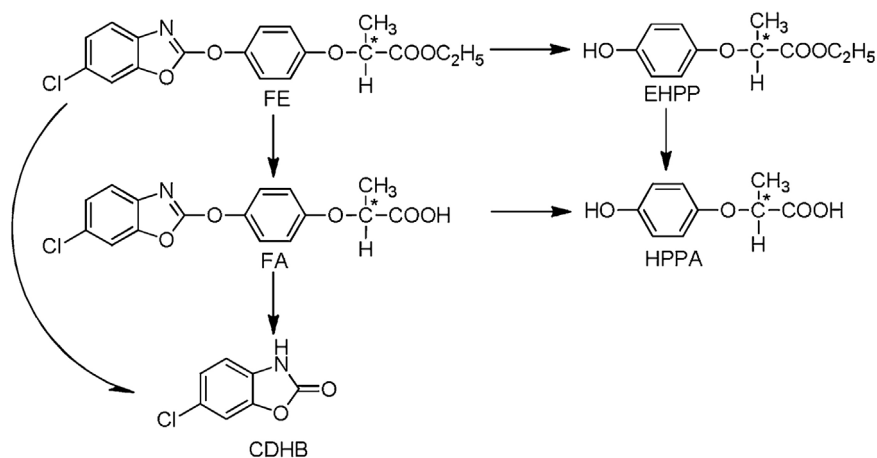


Fig. 1. Chemical structures of FE and its metabolites. Asterisk (*) denotes chiral center.

grasses (Pornprom et al., 2006). It has been widely used in many counties with annual sales of more than 200 million US dollars. With respect to its environmental fate, the primary degradation pathway of FE was hydrolysis and the main degradation product was fenoxaprop (FA, Fig. 1), which also has herbicidal activity as much as one hundred times more effective than fenoxaprop-ethyl in inhibiting grass chloroplasts ACCase (Lin et al., 2007). The metabolite FA can also inhibit seed germination of various grass weeds (Hoagland and Zablutowicz, 1998). Broad leaf herbicides such as 2,4-dichlorophenoxyacetic acid and 2-methyl-4-chlorophenoxy acetic acid can be mixed with FA to better ensure the safety of crops (Singh et al., 2013). It has been reported that FA was generated in microorganisms, soil, rice, wheat, barley, crabgrass, soybean, and so on (Chen et al., 2011; Hoagland and Zablutowicz, 1998; Lucini and Pietro Molinari, 2010; Tal et al., 1993). Forty days after field application, FA was still detectable in soil. Although the degradation of FE in soils, plants and animals has been reported (Chen et al., 2011; Lucini and Pietro Molinari, 2010), a little attention has been devoted to their enantioselective degradation. Enantioselective behavior of FE and FA in soils and rabbits has been studied with S-form being degraded faster than R-form (Zhang et al., 2011; Zhang et al., 2010). Stereoselective environmental behavior of FE and its chiral metabolites deserves enough attentions.

Because of the fast dissipation of FE (Chen et al., 2011; Zhang et al., 2011; Zhang et al., 2010), metabolites are important to consider as well during the process of environmental risk assessment. At present, studies on the metabolites of FE mainly focus on chiral FA and achiral 6-chloro-2,3-dihydrobenzoxazol-2-one (CDHB, Fig. 1), whereas information regarding chiral ethyl-2-(4-hydroxyphenoxy)propanoate (EHPP, Fig. 1) and 2-(4-hydroxyphenoxy)propanoic acid (HPPA, Fig. 1) is relatively much less (Chen et al., 2011; Lucini and Pietro Molinari, 2010; Zhang et al., 2010). It is worth noticing that very little information about enantioselective toxicity of FE and its three chiral metabolites has been known (Zhang et al., 2008). FE is one of the most commonly used post-emergence herbicides and large amounts of FE residues in soil, resulting in potential damage to the soil ecosystem such as the non-target organism earthworm. To our knowledge, it has not been reported that the enantioselective toxicity and degradation of FE and its metabolites in the ecological indicator earthworm. In recent years, the enantioselective fate and toxicity of chiral pesticides in earthworm has been studied to develop optically pure pesticides with high efficiency and low toxicity (Katagi and Ose, 2015), such as insecticides (fipronil, alpha-hexachlorocyclohexane, alpha-cypermethrin,

fenvalerate, bifenthrin, lambda-cyhalothrin, methamidophos and cycloxyprid), fungicides (metalaxyl, benalaxyl, furalaxyl, diniconazole, tebuconazole, myclobutanil, hexaconazole, epoxiconazole and tetraconazole) and herbicides (metolachlor and quizalofop-ethyl). Results indicated that chiral pesticide such as fungicide R-metalaxyl not only was more active than the S-metalaxyl but also exhibited lower toxicity and bioaccumulation to earthworm. To evaluate the impacts of chiral pesticides on soil animals, enantioselectivity and metabolites should be considered for accurate environmental risk assessment.

FA is a primary metabolite of FE, CDHB, EHPP and HPPA are also reported metabolites of FE, in which FA, EHPP and HPPA are chiral. In the study, the earthworm was exposed to FE under laboratory condition in natural soil to invest the degradation in earthworm. FE and its four metabolites were measured and the stereoselective behavior of FE and FA was also determined. Enantiomer-specific acute toxicity of FE and its metabolites were measured by the filter paper contact assay.

2. Materials and methods

2.1. Chemicals and materials

Racemic FE (>98.0% purity) was obtained from Institute for Control of Agrichemicals, China Ministry of Agriculture (Beijing, China). Racemic FA, EHPP and HPPA, the two enantiomers of FE, FA, EHPP and HPPA (>98.0% purity) were synthesized according to the reported methods (Amabilino et al., 1998; Kato et al., 2004; Moon et al., 2007). CDHB (>98.0% purity) was obtained from TCI Development Company Limited (Shanghai, China). Standard solutions were prepared in acetone at 1000 $\mu\text{g mL}^{-1}$ and kept in darkness at 4 °C. Water was purified by a Milli-Q system. Methanol (HPLC grade) was bought from Fisher Scientific (Fair Lawn, NJ, USA). All other chemicals and solvents were bought from Beijing Chemical Reagent Company Limited (Beijing, China) and were of analytical grade.

Mature earthworms (*Eisenia fetida*) were obtained from a farm on the outskirts of Beijing and 7-days preculture was conducted to make earthworms to adapt to the experimental conditions. The earthworms were healthy and active before introduced to the experiment. The weights of earthworms were 0.35 ± 0.03 g and the lengths were 5.0 ± 0.5 cm.

The soil was sampled at Baiwang Mountain Forest Park (Beijing, China). The soil was sieved, air-dried at room temperature. The soil composed by clay, 3.4%; silt, 36.2%; sand, 60.4%; organic matter, 4.7%, and the pH value was 7.6. FE and its metabolites were not detected in earthworm or soil.

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