



Degradation of chiral neonicotinoid insecticide cycloxaprid in flooded and anoxic soil



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HIGHLIGHTS

- CYC showed the short persistence in the submerged and anoxic soils.
- CYC produces a series of transformation products affected by soil properties.
- Stereoselective degradation pathways between two CYC enantiomers were not observed based on the experimental data.
- The time-dependent dynamic changes of CYC transformation products were explained.

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ABSTRACT

Cycloxaprid (CYC), with two stereogenic centers from oxabridged ring, is a novel potent neonicotinoid insecticide. The investigation of relevant transformation products (TPs) is critical for the risk evaluation of CYC on environment impact and further regulatory decisions. In this study, stereoselective soil metabolism of CYC enantiomers was investigated using isotope labeling techniques. Liquid scintillation counting with LC–MS/MS was used to identify and quantify the major transformation products (TPs) of CYC enantiomers in four various soils under anoxic and flooded condition. Most of CYC had been transformed in four soils at 5 d after treatment. Furthermore, CYC was found converted to a range of transformation products, which exhibited soil-specific dynamic changes. Cleavage of the oxabridged seven-member ring, reductive dechlorination in the chloropyridinyl and cleavage of C–N between the chloropyridinylmethyl and imidazolidine ring are the main transformation pathways of CYC. It is presumed that acidic condition may conduce to form the cleavage product of oxabridged seven-member ring. However, abiotic or biotic stereoselective persistence of TPs in all soils was not observed from the experimental data and may be attributed to the unstable oxabridged ring.

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1. Introduction

Neonicotinoids, the most important class of synthetic insecticides of the past decades, have outstanding potency in crop protection against piercing-sucking pests. Imidacloprid (IMI), nitenpyram, acetamiprid, thiacloprid, thiamethoxam, and others neonicotinoids act as agonists at the insect nicotinic acetylcholine receptor (nAChR) (Tomizawa and Casida, 2003). These nAChR agonists are highly versatile in terms of application methods and they can be

used with a wide range of different application techniques including foliar, seed treatment, soil drench, and stem application with several crops (Jeschke et al., 2013). With the frequent field application of these insecticides, the increasing resistance and cross-resistance have been observed in several species (Reyes et al., 2007). Although neonicotinoids insecticides have been used for decades, the relevant knowledge of environment behavior of neonicotinoids insecticides is very incomplete (Dick et al., 2006; Ford and Casida, 2006a,b, 2008; Karmakar et al., 2009; Žabar et al., 2011). For instance, widespread declines of wild and managed insect pollinators caused the discussion on neonicotinoids insecticides recently (Cameron et al., 2011; Cresswell and Thompson, 2012; Henry et al., 2012; Osborne, 2012).

Cycloxaprid (CYC), a novel *cis*-nitromethylene neonicotinoid insecticide, displays a 50-fold higher activity against IMI-resistant

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brown planthopper than IMI (Shao et al., 2010, 2011a,b, 2013). CYC has already obtained joint efforts aiming at commercialization from ECUST, Shanghai Shengnong Pesticide Co., Ltd. Therefore, the investigation of relevant transformation products (TPs) is critical for the risk evaluation of CYC on environment impact and further regulatory decisions.

CYC, with two stereogenic centers, has an oxabridged ring and consists of two stereoisomers. About 25% of currently used pesticides are chiral, such as dichloroprop, mecoprop, metolachlor, bifenthrin, fonofos, malathion (Lewis et al., 1999). These structures usually have one or two chiral carbon, sulfur, phosphorus atom (Hegeman and Laane, 2001). In many cases, exposure of racemic insecticides to natural environment, in either field applications or laboratory microcosms, results in selective microbial degradation of one of the enantiomers. To our knowledge, enantiomers often exhibit different effects or toxicity, and may even have adverse effects on some nontarget species (Kallenborn and Hühnerfuss, 2001; Buerge et al., 2003, 2006, 2012; Liu, 2005; Sekhon, 2009; Ye et al., 2010). Consequentially, several single- or enriched enantiomer pesticide formulation have been developed and promoted in North America and Europe (Buser and Müller, 1998; Roberts and Hutson, 1999). The environmental fate of CYC's enantiomers also absorbed our attention.

Previous bioassays have shown that the two stereoisomers of CYC were endowed with nearly identically excellent insecticidal activities against alfalfa aphids. However, the relevant metabolites information of CYC in environment remains unknown. Hence, the transformation products and pathway of two CYC enantiomers in environment soil should be clarified before extensive application.

In this study, considering that CYC is usually sprayed into paddy fields, ^{14}C -labeled CYC enantiomers were incubated in four flooded and anoxic soils. Liquid chromatography–tandem mass spectrometry (LC–MS/MS) was used in collaboration with ^{14}C tracer technique to identify the transformation products and track the dynamics changes of single enantiomer of CYC.

2. Materials and methods

2.1. Chemicals

[$^{14}\text{C}_2$]-CYC, 5-((6-Chloro-pyridin-3-yl)methyl-7-nitro-11-oxa-2,5-[$^{14}\text{C}_2$]diazatricyclo[6.2.1.0^{2,6}]undec-6-ene (^{14}C -CYC), was synthesized by ourselves in the lab and the position of the ^{14}C labeling were seen in the Fig. 1 (Li et al., 2011a,b, 2012). (1S2R)- ^{14}C -labeled CYC (SR), (1R2S)- ^{14}C -labeled CYC (RS) and the racemic mixture (RM) (radiochemical and chemical purity >99%, 0.69 mCi mmol⁻¹) were separated by HPLC using DAICEL CHIRALPAK IC column (5 μm , 30 \times 250 mm, DAICEL Chiral Technologies, Tokyo, Japan). Scintillation cocktail A was prepared by dissolving 0.5 g of 1,4-bis-(5-phenyloxazol-2-yl)-benzene (POPOP, Arcos Organics, Geel, Belgium) and 7.0 g of 2,5-diphenyloxazole (PPO, Arcos Organics, Geel, Belgium) in 350 mL of 2-methoxyethanol and 650 mL of dimethylbenzene. Scintillation cocktail B was prepared by dissolving 0.5 g of 1,4-bis-(5-phenyloxazol-2-yl)-benzene (POPOP, Arcos Organics, Geel, Belgium) and 7.0 g of 2,5-diphenyloxazole (PPO, Arcos Organics, Geel, Belgium) in 225 mL of 2-methoxyethanol, 600 mL of dimethylbenzene and ethanolamine (175 mL). All solvents and chemical reagents used were of high-performance liquid chromatography grade.

2.2. Soils

Three experimental soils were collected from surface layer (0–15 cm) of farmland in different zone of Zhejiang Province, China. Fine coastal saline soil from Cixi, fluvio-marine yellow

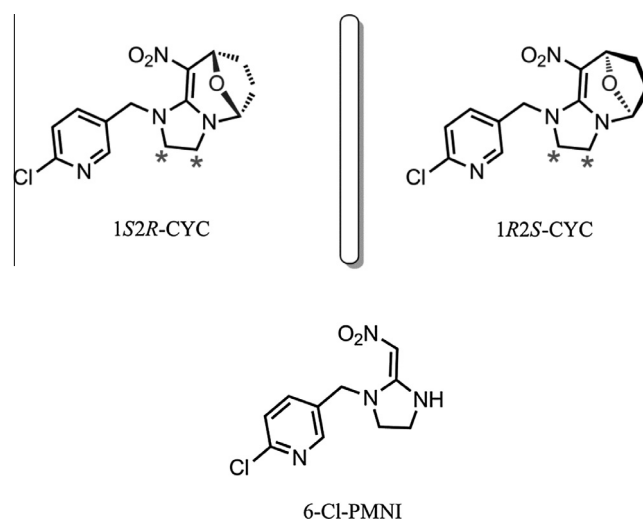


Fig. 1. Structures of the 1S2R-CYC, 1R2S-CYC and 6-Cl-PMNI, with asterisks marking the position of ^{14}C labeling in 1S2R-CYC, and 1R2S-CYC.

loamy soil from Hangzhou and red-clayed soil from Longyou are represented herein by S1, S2 and S4, correspondingly. All sampled soils were air-dried, crushed, mixed, and screened through a 1-mm sieve in advance.

In order to investigate the role of microorganism in degradation of CYC enantiomers, a subsample of soil S2 was sterilized by ^{60}Co γ -irradiation at an absorbed dose of 20 kGy (dose rate 1.25 kGy h⁻¹) for 12 h, and then sodium azide (500 mg L⁻¹) was added to inhibit microbial growth. The subsample soil was represented by S3. Selected physicochemical characteristics of the soils were determined by standard methods and are given in Table 1 (Nelson and Sommers, 1982; Gee and Bauder, 1986).

2.3. Incubation experiment and pretreatment

The incubation experiment and treatment under the anoxic and dark condition, using ^{14}C -SR-CYC, ^{14}C -RS-CYC and ^{14}C -RM-CYC in four flooded soils were performed based on a modified OECD (Organization for Economic Co-operation and Development) Guideline for the Testing of Chemicals (OECD 307). In brief, 24 mg of each ^{14}C -CYC in stock solution were applied to the single soil (20 g, dry weight) for ^{14}C -SR-CYC, ^{14}C -RS-CYC and ^{14}C -CYC racemic mixtures (RM) respectively, and the applied soil was stirred well to ensure all the carrier solvent was evaporated. The treated soil was then diluted with the same type of soil (160 g, dry weight) in a fume hood to attain a certain concentration of 10 mg kg⁻¹ and the radioactivity of 8.33 MBq kg⁻¹. The homogeneity of ^{14}C distribution was verified by combustion of three ^{14}C soil subsamples on a biological oxidizer (OX-600, R.J. Harvey Instrument, Hillsdale, NJ, USA) and analyzing the trapping $^{14}\text{C}\text{O}_2$ in cocktail B by LSC (recovery 95.3 \pm 4.2%). A 10 g (dry weight) aliquot of the applied soil was subsequently transferred into a 30-mL glass vial and immersed by 12 mL distilled water. All the uncovered vials were moved into incubation vessels which were connected to a series of air-tight test tubes, which allowed for entrapment of ^{14}C volatile organic compounds and $^{14}\text{C}\text{O}_2$. At different interval of 5, 10, 20, 30, 45, 60, 80, 100 d of incubation, the soil–water subsamples (10.0 g dry weight equivalent) of soil were sequentially extracted with 0.01 M CaCl₂, acetonitrile/water (9:1, v/v), methanol until no detectable radioactivity was found in additional extraction. Each treatment was replicated three times. All extractions were combined and condensed on the vacuumed rotary

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