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Non-stereoselective transformation of the chiral insecticide cyclozaprid in aerobic soil

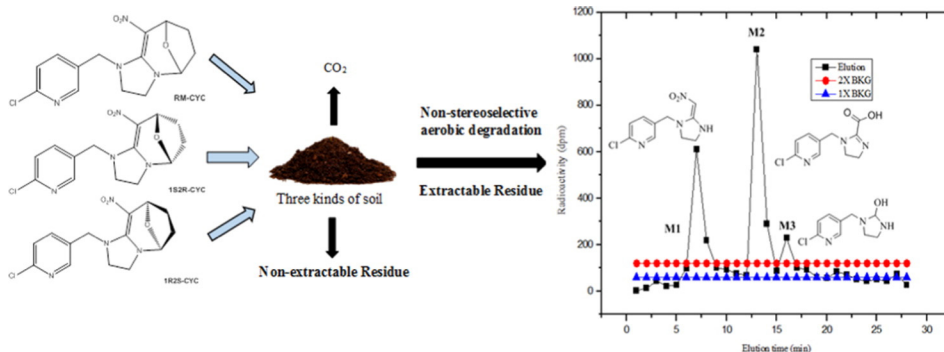
Min Chen¹, Yupeng He¹, Yatian Yang, Lei Huang, Hanxue Zhang, Qingfu Ye, Haiyan Wang*

Institute of Nuclear Agricultural Sciences, Key Laboratory of Nuclear Agricultural Sciences of Ministry of Agriculture and Zhejiang Province, Zhejiang University, Hangzhou 310029, China

HIGHLIGHTS

- Cyclozaprid degraded very quickly in aerobic soils.
- Three degradation intermediates were identified by ¹⁴C labeling and LC-QTOF-MS/MS.
- No stereoselective degradation was observed for cyclozaprid isomers.
- We clarified soil-specific changes of CYC intermediates over time.

GRAPHICAL ABSTRACT



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ABSTRACT

Cyclozaprid (CYC) is one of the most effective neonicotinoid insecticides and is proposed to be a replacement of imidacloprid that has caused concerns over non-targeted resistance and ecological toxicity worldwide. The present study was performed with the ¹⁴C-labeled racemic CYC and its two enantiomers in aerobic soil. Racemic CYC and the enantiomers 1S2R-CYC and 1R2S-CYC underwent non-stereoselective degradation in the three soils tested. During the incubation period, CYC was transformed into three achiral degradation products which displayed varying degradation kinetics dependent upon soil properties. The soil properties were found to significantly influence the CYC metabolite profiles. The fastest degradation occurred in loamy soil, whereas the slowest reactions occurred in acidic clay soil. The primary transformation of CYC included cleavage of the oxabridged seven-member ring and C–N between chloropyridinylmethyl and imidazolidine ring, carboxylation of the alkene group, and hydroxylation of imidazolidine ring. The results shed light on understanding of CYC degradation and provided useful information for applications and environmental assessments of chiral pesticides.

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1. Introduction

Neonicotinoid insecticides were first introduced in the 1990s. They are agonists acting on insect nicotinic acetylcholine receptors with little harm to mammals (Tomizawa and Casida, 2003). They occupied 24% of the total market of insecticides (Jeschke et al., 2011). The most commonly used neonicotinoids are thiamethoxam, clothianidin, and

* Corresponding author.

E-mail address: wanghaiyan@zju.edu.cn (H. Wang).

¹ These authors contributed equally to this work.

imidacloprid which have been registered in 120 countries and used to 295 crops (Elbert et al., 2008). However, exposure to those neonicotinoids could unintentionally reduce crop yield (Douglas et al., 2015), and has been linked to the decline in bee populations (Gill et al., 2012; Henry et al., 2012; Kessler et al., 2015), disorder of bee colonies (Whitehorn et al., 2012), and decline in the number of insectivorous birds (Goulson, 2014; Hallmann et al., 2014). In 2013, the European Commission (including member countries of the Organization for Economic Co-operation and Development, OECD) prohibited the use of the three insecticides that might affect the life cycle of bees, but have positive agricultural benefits (OECD, 2013). The growing insect resistance and the poison to bees, birds and crops of neonicotinoid insecticides lead to an urgent need to assess their environmental risk.

Cycloxaprid (CYC), a chiral oxabridged cis-configuration neonicotinoid insecticide, has two stereogenic centers and an oxabridged ring with two stereoisomers of 1R, 2S and 1S, 2R configurations (Fig. 1). CYC manifests >50 times effective than imidacloprid against imidacloprid-resistant brown plant-hopper (Shao et al., 2010). CYC had good contact and root-systemic activity (Cui et al., 2012). Shao et al. (2013) found that the in-vitro site affinity of imidazole to nicotinic acetylcholine receptors in house flies, honeybees, and mouse brain membranes was 15–40 times stronger than that to CYC. In recent years, chiral pesticides have attracted great attention because many biological activities are generally stereoselective to these compounds, and biologically mediated environmental processes could also exhibit isomer selectivity. Chiral pesticides are commonly used as racemic mixtures and their stereoisomers are often degraded stereoselectively in soils (Williams, 1996; Kurihara et al., 1997; Liu et al., 2005a & b; Garrison, 2006; Fu et al., 2015). Stereoisomers of chiral pesticides may manifest different bioactivities and toxicities to biota (Liu et al., 2005a & b). For example, Li et al. (2012) reported preferential degradation of (–)-S-tetraconazole over (+)-R-tetraconazole in plants, and non-stereoselective degradation of tetraconazole in soils. Zhang et al. (2013) observed stereoselective uptake and translocation of CYC in edible vegetables from roots, but minimum amount in vegetables from foliar applications. Pan et al. (2016) found apparent stereoselective dissipation of novel chiral fungicide pyrisoxazole in cucumber and tomato after both root and foliar applications, but little stereoselectivity was observed for its degradation in soils.

Previous studies reported that approximately 80–90% of neonicotinoids are persistent in soils after seed coating applications, and the corresponding half-lives varied in different soils (Goulson, 2014). Liu et al. (2015) identified and tracked 11 transformation products of CYC, and tracked their changes with time in flooded and anoxic

soils. However, little is known on the degradation of chiral CYC in aerobic soil. The present study was to use ^{14}C -labeled CYC to characterize the transformation kinetics and products, to evaluate persistence of individual CYC stereoisomers and racemates in the three soils under aerobic condition, and elucidate the degradation pathways with focus on the effects of stereoselectivity on their dissipation.

2. Materials and methods

2.1. Insecticides and chemicals

A racemic mixture of ^{14}C -labeled CYC (5-((6-chloro-pyridin-3-yl)methyl-7-nitro-11-oxa-2,5-[$^{14}\text{C}_2$]diaz-tricyclo[6.2.1.0 2,6]undec-6-ene was synthesized by East China University of Science and Technology, and Zhejiang University (Li et al., 2011a). The specific activity of ^{14}C -labeled CYC was $8.029 \times 10^4 \text{ Bq mg}^{-1}$, and the radiochemical and chemical purities were both >98%. The purity of CYC was determined with high performance liquid chromatography (HPLC). The radiochemical purity was determined with HPLC-liquid scintillation counting (LSC) detection and thin layer chromatography-isotope imaging analysis (Yang et al., 2009; Liu et al., 2011). The stereoisomers of ^{14}C -CYC were separated by preparative HPLC with a Daicel Chiralpak IC column (Li et al., 2013). The ^{14}C -labeling positions and the two enantiomers were shown in Fig. 1.

Acetonitrile, methanol and acetic acid were HPLC grade. The other solvents and chemicals such as glycol ether, dimethylbenzene and ethanol were analytical grade. The scintillation cocktails were 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) in 350 mL of 2-ethoxyethanol and 650 mL of dimethylbenzene.

2.2. Experimental setup

Three natural soils that had not previously been treated with CYC were collected from the 0–15 cm top layer of agricultural fields in Hangzhou (fluvio-marine yellow loamy soil), Cixi (coastal saline soil), and Longyou (red clay soil), Zhejiang Province, China. These soils were abbreviated as H, C, and L in this study, respectively. Selected physico-chemical properties of the three soils were listed in Table 1. The soils were air dried, filtered through a sieve (2 mm) to remove plant debris, and then stored at room temperature in the dark.

Incubation experiments were performed to investigate environmental behaviors of enantiopure enantiomers (1S2R-CYC and 1R2S-CYC) and their racemate (RM-CYC) in the three soils based on the method of OECD Guideline 307 (2002). Soil moisture content was adjusted to 50% of water-holding capacity during the experiment. Each soil was incubated for two weeks at 25 °C in a cultivation cabinet in dark to re-establish soil microbial communities. An aliquot of CYC stereoisomer stock solution (10 mL) containing 50% ^{14}C -labeled and 50% non-labeled CYC in acetonitrile with the total concentration of 0.5 mg mL^{-1} was dropwise spiked in 50 g of soil (dry weight). The soil sample was mixed thoroughly using a spatula, followed by evaporation of the

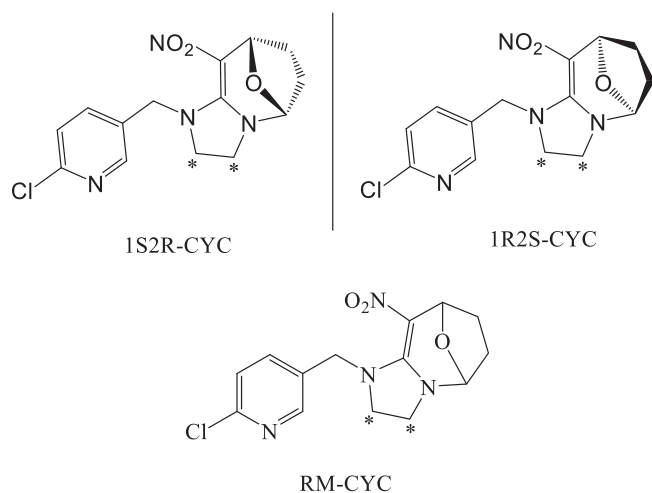


Fig. 1. Structures of ^{14}C labeled 1S2R-CYC, 1R2S-CYC and RM-CYC with asterisks indicating ^{14}C positions.

Table 1
Physico-chemical characteristics of three soils.

Soil site	Soil texture	pH ^a	OM ^b (g·kg ⁻¹)	CEC ^c (cmol·kg ⁻¹)	Particle size (%)		
					Clay	Silt	Sand
Longyou (L)	Red clay soil	4.2	7.8	6.62	39	41	20
Hangzhou (H)	Fluvio-marine yellow loam soil	7.0	30.5	10.83	8	71	21
Cixi (C)	Coastal saline soil	8.8	24.8	10.17	24	71	5

^a Suspension of soil in water.

^b Organic matter.

^c Cation exchange capacity.

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