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Stereoselective environmental behavior and biological effect of the chiral organophosphorus insecticide isofenphos methyl

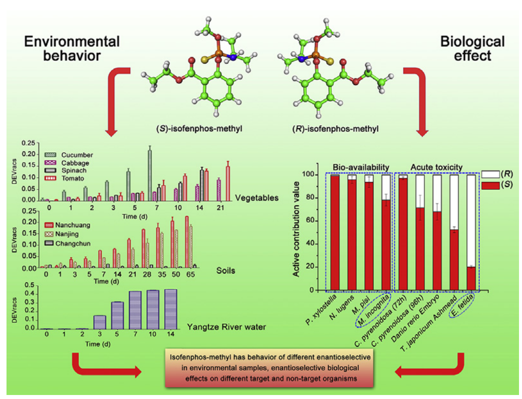
Beibei Gao [a], Zhaoxian Zhang [a], Lianshan Li [a], Amir E. Kaziem [a,b], Zongzhe He [a], Qianwen Yang [a], Peiyang Qing [a], Qing Zhang [a], Minghua Wang [a,*]

[a] Department of Pesticide Science, College of Plant Protection, Nanjing Agricultural University, State and Local Joint Engineering Research Center of Green Pesticide Invention and Application, Nanjing, Jiangsu 210095, China
[b] Department of Environmental Agricultural Science, Institute of Environmental Studies and Research, Ain Shams University, Cairo 11566, Egypt

HIGHLIGHTS

- (*S*) isofenphos methyl exhibits more bioactivity in the range of 2.8–150 times.
- (*S*) form has more acute toxicity to all the selected organisms except *E. foetida*.
- (*R*) isofenphos methyl degraded faster in all the selected vegetables.
- (*R*) isofenphos methyl degraded preferentially in Yangtze River water.
- (*S*) isofenphos methyl degraded preferentially in Nanjing and Nanchang soils.

GRAPHICAL ABSTRACT



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ABSTRACT

The enantiomeric environmental behaviors, bioactivities and toxicities of isofenphos methyl enantiomers were characterized systematically in this study. (*R*) Isofenphos methyl was degraded preferentially in Yangtze River water and different types of vegetables with an enantiomeric fraction (EF) of 0.6 to 0.96. However, (*R*) isofenphos methyl was amplified in both Nanjing (EF = 0.32) and Nanchang (EF = 0.27) soil. Our investigations found that there no bidirectional chiral inversion occurred in either Yangtze River water or soils. The bioactivity of (*S*) isofenphos methyl was higher than that of its (*R*) enantiomer against different insect targets, such as *Meloidogyne incognita*, *Nilaparvata lugens*, *Plutella xylostella* and *Macrosiphum pisi* (3.7 to 149 times). (*S*) Isofenphos methyl showed higher toxicity for the nontarget organism (1.1 to 32 times). However, (*R*) isofenphos methyl possesses 4.0 times more potency than the (*S*)-form for the nontarget soil organism *Eisenia foetida*. This study generally could provide more scientific guidance for the corresponding risk assessments of pesticides in addition to providing a new theoretical basis for scientifically and rationally using isofenphos methyl.

1. Introduction

As one of the important agrochemical classes, chiral pesticides are applied extensively in agricultural pest management. Approximately

* Corresponding author.
E-mail address: wangmha@njau.edu.cn (M. Wang).

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30%–40% of pesticides in China have asymmetric centers, which include several enantiomers (Ye et al., 2015; Zhao et al., 2014). Chiral enantiomers have similar physicochemical properties. Behaviors, bioactivities, toxicities, biodegradation rates and kinetics of the chiral pesticides showed dramatic difference in the chiral environment (Dong et al., 2013; Konwick et al., 2006; Liu et al., 2005; Ye et al., 2010; Yao et al., 2016; Zhang et al., 2018). Organophosphorus compounds are the most widely used agrochemicals against agricultural pests. More than 40 million kilos are used annually in the United States (Mulchandani et al., 1999), which resulted in serious contamination from organophosphorus compounds in water and terrestrial ecosystems (Kim et al., 2013; McKone et al., 2007; Singh and Walker, 2006; Sun et al., 2011; Zhou et al., 2009). Approximately 300,000 deaths occur annually in the developed world and low-resource regions due to OP poisoning (Roberts and Aaron, 2008; Lee et al., 2013). The commercial organophosphorus agrochemicals in the world (approximately 55 of 149 are chiral) pose great risks for the environment due to their widespread use in agricultural management (Qiu, 2014; Sun, 2015). Enantiomers of chiral organophosphorus compounds show dramatic enantioselectivities. This property includes the (+) enantiomer of isofenphos and its metabolite isofenphos oxon, which has more potency than the (−) enantiomers on *Musca domestica* and *Callosobruchus chinensis* (Ueji and Tomizawa, 1986). The (−) methamidophos is approximately 8.0–12.4 times more toxic for the acetylcholin esterase (AChE) of bovine erythrocytes and *Electrophorus electricus* than its (+)-form (Lin et al., 2006). The (*R*) (+) methamidophos is enriched in Zhengzhou soil (loam) but degrades faster than the (*S*) (−) methamidophos in Changchun (silt loam) and Nanchang (sandy clay) soils (Wang et al., 2013). To date, no chiral OPs have been applied in agriculture in their enantiopure form. This knowledge gap between the widely varying chiral phenomena and the regulations of chiral OPs as achiral compounds constitutes a considerable risk.

As a typical chiral organophosphorus pesticide, isofenphos methyl has one asymmetric phosphorus atom and presents a pair of enantiomers, as shown in Fig. S1. Isofenphos methyl presents a broad lethal spectrum and high insecticidal effects. However, isofenphos methyl has some challenges due to its high toxicity and long-lasting effects. Xu et al. reported that isofenphos methyl was detected in 32 of 40 Yancheng vegetables samples, with a rate of 80% (Xu et al., 2017). Only two methods for the enantioselective separation and determination of isofenphos methyl have been reported to date (Chen et al., 2016; Gao et al., 2016). There is no research reporting the enantioselective activity or toxicity of isofenphos methyl on target or nontarget organisms. Regarding the stereoselective behavior of the isofenphos methyl enantiomers, previous research demonstrated that (*S*) isofenphos methyl is more stable than (*R*) isofenphos methyl in *Brassica chinensis L.* Considering the enantioselective degradation of isofenphos methyl enantiomers in *Brassica chinensis L.* (Gao et al., 2016) and the distinct differences in the bioactivities and toxicities of chiral organophosphorus enantiomers, a systemic study that focused on the isofenphos methyl enantiomers and their relative bioactivity, toxicity, and environmental behaviors is urgently needed.

This study was conducted for the following research questions. First, does the dissipation behavior of isofenphos methyl enantiomers in *Brassica chinensis L.* also exist in other plants and environmental samples? Second, are there any different enantioselective biological effects between the isofenphos methyl enantiomers on different target and nontarget organisms? The environmental behaviors of isofenphos methyl racemic and the optically pure isofenphos methyl enantiomers were studied in this paper in water and soil samples under unsterilized and sterilized conditions. The degradation of isofenphos methyl in water and soils were studied at different periods to understand the processes involved in enantioselective dissipation more clearly. In addition, the stereoselective dissipation of isofenphos methyl in vegetables was also investigated. Different invasive pests and nontarget insects were used to investigate the enantioselective biological effect.

2. Materials and methods

2.1. Materials

The (*Rac*) isofenphos methyl standard (≥98.1%) was obtained from Shanghai Pesticide Research Institute Co., Ltd. (Shanghai, China). The optically pure enantiomers (≥99.39%) were prepared by Chiralway Biotech Co., Ltd. (Shanghai, China). HPLC-grade acetonitrile and methanol were purchased from TEDIA (Fairfield, USA). Purified water was obtained using MUL-9000 water purification systems (Nanjing Zongxin Water Equipment Co. Ltd., China). The 0.22-μm filter membranes were bought from ANPEL Laboratory Technologies Co., Ltd. (Shanghai, China). Cleanert-Florisil (500 mg, 6 mL) and Alumina-A (1000 mg, 6 mL) were obtained from Agela Technologies (Tianjin, China). Other chemicals of analytical grade were purchased from commercial sources.

2.2. Stereoselective degradation in Yangtze River water

Water samples (pH = 6.7) collected from the Yangtze River (Nanjing, China) were incubated at room temperature for one week before the racemic and enantiopure isofenphos methyl were spiked at 4 mg L^{-1}. The sterilized water went through 20 min of 121 °C moist heat sterilization, with the same concentration of unsterilized water set as a control. The samples were incubated in the dark at 25 °C. The samples were collected at 2 h, 1–90 d after treatment and stored at −20 °C. The concentrations of isofenphos methyl enantiomers were analyzed in the same batch after all samples had been collected.

2.3. Soil collection and soil incubation experiments

Soil samples were collected from the cultivation areas of Jiangsu Province (Nanjing), Jiangxi Province (Nanchang), and Jilin Province (Changchun) in China from the top 0–10 cm of soil. The physicochemical characteristics were tested and listed in Table S1. All soil samples were air dried at room temperature and sieved to <2 mm. The sterilized soils were obtained after two periods of 60 min, 121 °C moist heat sterilization with a 24 h interval between autoclave treatments. In the soil incubation, Nanjing soil in triplicate were spiked with racemic and enantiopure isofenphos methyl, and Jiangxi and Changchun soil were spiked with *Rac* isofenphos methyl at 4 mg kg^{-1} to study the degradation tendency. Ten grams of thoroughly mixed soil were added to a 50 mL threaded tube; the moisture content was adjusted to 60% using sterilized water or 0.2% sodium azide solution (for sterilized soils) and sealed with foam plugs. All treated soil samples were incubated at 25 °C in the dark. The samples were collected at 2 h, 1–60 d after incubation and stored at −20 °C. The concentrations of isofenphos methyl enantiomers were analyzed in the same batch after all samples had been collected.

2.4. Field experiments

Experimental fields for the enantioselective dissipation studies in vegetables (spinach, cabbage, cucumber, and tomato) were divided into 30-m^2-sized blocks with corresponding buffer zones in Nanjing, China. A 40% isofenphos methyl emulsifiable concentrates was diluted and sprayed on the tested vegetables at dosages of 500 g.a.i. ha^{-1} (spinach, cabbage) and 1000 g.a.i. ha^{-1} (cucumber, tomato), respectively. Samples were collected at 2 h and 1, 3, 5, 7, 10, 14, 21 and 28 days after spraying and stored at −20 °C. The concentrations of isofenphos methyl enantiomers were analyzed in the same batch after all samples had been collected.

2.5. Analysis of soil and environmental samples

The isofenphos methyl enantiomers were determined according to methods described by (Gao et al., 2016). In short, 20 g of vegetable