Chemosphere 147 (2016) 287–296

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Degradation properties and identification of metabolites of 6-Cl-PMNI in soil and water

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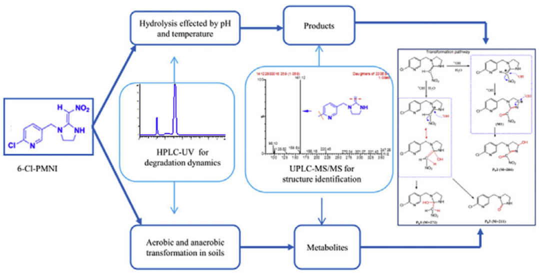
HIGHLIGHTS

- 6-Cl-PMNI is stable in room temperature and neutral media.
- Temperature is the main fact which influences the hydrolysis of 6-Cl-PMNI.
- The C=C olefinic bond reacted with H_2O may be the main hydrolytic mechanism.
- 6-Cl-PMNI can be readily degraded in soil mainly by microbial action.
- The split of C–Cl is proposed as the degradation pathway of 6-Cl-PMNI in soil.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 30 August 2015
Received in revised form
29 November 2015
Accepted 4 December 2015
Available online 14 January 2016

Handling Editor: Klaus Kümmerer

Keywords:
6-Cl-PMNI
Degradation half life
Water
Soil
Metabolite

ABSTRACT

In order to provide the scientific basis for the environmental risk assessment of cycloxaprid and 6-Cl-PMNI (intermediate of cycloxaprid), the degradation properties of 6-Cl-PMNI in aerobic, anaerobic and/or sterile soil, as well as in water with different pH values at different temperature were explored under laboratory conditions using HPLC for its kinetics study and UPLC-MS/MS for the identification of its metabolites/degradation products. Fortification study showed that the recoveries of 71.4–100.5% with the maximum coefficient variation (CV) of 7.47% were obtained. The linear range was 0.1–10 mg/L with the good linearity of $R^2 = 0.9990$. For standard, the method LOD (limit of detection) and LOQ (limit of quantification) was 0.03 mg/L and 0.1 mg/L, respectively. Results demonstrated the good performance of the developed method. Kinetics study indicated that the degradation half-lives ($t_{0.5}$) in pH 3-pH 10 buffers varied from 111.8 d to 288.8 d at 25 °C but rapidly shortened to 1.6–25.7 d at 70 °C. Good negative linear ships ($R^2 \geq 0.8423$) between half life and temperature were found. 6-Cl-PMNI could be readily degraded in non-sterile soil ($t_{0.5}$ 0.8–7.5 d) while slowly degraded in sterile soil ($t_{0.5}$ 64.8–91.2 d). Three hydrolytic products and one metabolite of 6-Cl-PMNI in aerobic soil were identified. The C=C olefinic bond reacted with H_2O by Markovnikov Additive Reaction and the split of C–Cl were mainly proposed as the possible reaction pathway for 6-Cl-PMNI degradation in water and in soil, respectively.

Abbreviations: 6-Cl-PMNI, 2-chloro-5-[[2- (nitromethy-l-ene)-1-imidazolidinyl] methyl] pyridine; CYC, cycloxaprid; HPLC, high performance liquid chromatography; UPLC-MS/MS, ultra performance liquid chromatography tandem mass spectrometry; LLE, liquid–liquid extraction; MLOD, limit of detection for standard; MLOQ, limit of quantification for standard; rpm, rotation per min; RT, retention time; OM, organic matter.

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http://dx.doi.org/10.1016/j.chemosphere.2015.12.020
0045-6535/

1. Introduction

Numerous drinking water sources and soils in the environment have been contaminated with pesticides, pharmaceuticals, plasticizers, and antimicrobial agents, as well as other potentially harmful chemicals (Kolpin et al., 2002 and Squillace et al., 2002). The fates of these compounds in environment are concerned due to the potential adverse health effects for organisms and ecological environment contaminated with numerous anthropogenic chemicals. Only five percent of active ingredient content can reach the target organisms when a pesticide is applied for crop protection and most parts of the content stay in soil and water for a long time as contamination (Van Eerd et al., 2003). Furthermore, enormous pesticides and its metabolites were discovered in the environment (Fenner et al., 2013). As known, the environmental behaviors such as photolysis, hydrolysis and soil degradation, and so on, have the giant influence on the fate and residue of pesticide in environment, which are also the indispensable link of pesticide registration and environmental safety evaluation.

Since the new neonicotinoid insecticides have been widely applied in agricultural production, the mode of action is highly regarded as a welcome new class chemistry owing to their high target specificity, low risk for non-target organisms and environment (Jeschke and Nauen, 2008). Cycloxaprid (CYC), 1-[(6-chloropyridin-3-yl)methyl]-9-nitro-2,3,5,6,7,8-hexahydro-1*H*-5,8-epoxyimidazo[1,2-a]azepine, one of the most effective neonicotinoid insecticides, was jointly developed in 2012 by East China University of Science and Technology (ECUST) and Shanghai Shengnong Pesticide Co., Ltd, China (Shao et al., 2011a, 2011b and Shao et al., 2013a, 2013b) and registered in China in 2015. The compound has excellent insecticidal activity for most homoptera pests and especially effective against imidacloprid (IMI)-resistant pests, which has a wide application prospects. Besides, it is also the first nicotinic acetylcholine receptors (nAChR) antagonist in the worldwide and likely to become a novel promising insecticide (Mori et al., 2002 and Cui et al., 2012). 6-Cl-PMNI, 2-chloro-5-[[2-(nitromethy-l- ene)-1-imidazolidinyl] methyl] pyridine, an intermediate of CYC, is one of common raw compounds to be used to synthesis neonicotinoid insecticides (Kagabu et al., 1992,Zapol'skii et al., 2009 and Liu et al., 2015). 6-Cl-PMNI is more potent agonists with insect than mammalian nAChRs (Tomizawa et al., 2000, Tomizawa and Casida, 2003), so it is also an ultra-high-potency neonicotinoid (Yamamoto and Casida, 1999). CYC can be prepared by adding succinaldehyde (Shao et al., 2010) to a highly potent insecticidal (nitromethylene) imidazole (6-Cl-PMNI) (Moriya et al., 1992) and can convert to 6-Cl-PMNI by hydrolysis (Fig. S1) (Shao et al., 2011a, b). It was demonstrated that CYC was a proinsecticide, chemically or metabolically converting to 6-Cl-PMNI and served as a slow-release reservoir for 6-Cl-PMNI when action for targeted insect. Previous bioassays showed that 6-Cl-PMNI was much more toxic than CYC for non-target organisms (Shao et al., 2013a). Moreover, it was said that the environmental risks of widely used neonicotinoid insecticides were underestimated in the past and more deep investigation should be done to prevent a similar mistake if the older insecticides be replaced with less toxic alternatives (Zeng et al., 2013). Hence, the fate of 6-Cl-PMNI, one of the important degradation products of CYC in environment should be clarified before extensive application. Up to now, the biological activity and chemical synthesis of 6-Cl-PMNI were paid close attentions, but there was few of report on the metabolism and degradation of 6-Cl-PMNI in environment (Shao et al., 2013a and Liu et al., 2015). At present, the degradations of 6-Cl-PMNI in the soil and water under different conditions were investigated in order to provide the scientific basis for the risk assessment of CYC and 6-Cl-PMNI and further regulatory decisions.

2. Experimental

2.1. Instrumentation and chemicals

The HPLC (high performance liquid chromatography) analysis was carried out on an Agilent 1260 Infinity LC system (Agilent, USA). The identification of metabolites or degradation products was performed by UPLC-MS/MS (Waters Acquity ultra-high performance liquid chromatography system coupled with a Waters Quattro Premier XE triple quadrupole mass spectrometer (Waters, Milford, MA, USA)). Constant temperature and humidity incubators were purchased from Xutemp Temptech Co. Ltd (Hangzhou, China). Super-clean bench was purchased from Antai Airtech Co. Ltd (Suzhou, China). Electronic analytical balance BSA123S was purchased from BSISL Co. Ltd (Beijing, China). pH meter PHS-3C was purchased from Instrument Science Co. Ltd (Shanghai, China). Centrifugation was performed in an Anke DL-5-B centrifugate (Shanghai Flying Pigeon, China). The rotary evaporator RE-2000 was purchased from Yarong Biochemical Instrument (Shanghai, China). Mechanical shaking extraction was performed by using a ZHWY-2012C constant temperature incubating shaker (Shanghai Zhicheng Analysis Instrument Manufacturing, China). Analytical Nitrogen Evaporator was purchased from Autoscience Co. Ltd (Tianjin, China). Water used in the test was ultrapure water which obtained from a water purification system (Pall Corporation, USA).

6-Cl-PMNI (98% of purity) standard was supplied from Shanghai Shengnong Pesticide Co., Ltd. All chemical reagents used were of analytical grade or better. Buffers with different pH were prepared as follows (U.S. EPA, 1998):

Buffer I (pH 3): 50.0 mmol potassium hydrogen phthalate (K_2HPO_4) and 20.3 mmol hydrochloric acid (HCl) were dissolved in water to form 1 L of aqueous solution;

Buffer II (pH 4): 50.0 mmol potassium hydrogen phthalate (K_2HPO_4) and 4.0 mmol sodium hydroxide (NaOH) were dissolved in water to form 1 L of aqueous solution;

Buffer III (pH 7): 50.0 mmol monopotassium phosphate (KH_2PO_4) and 29.6 mmol sodium hydroxide (NaOH) were dissolved in water to form 1 L of aqueous solution;

Buffer IV (pH 9): 25.0 mmol boric acid (H_3BO_3), 25.0 mmol potassium chloride (KCl) and 21.3 mmol sodium hydroxide (NaOH) were dissolved in water to form 1 L of aqueous solution;

Buffer V (pH 10): 50.0 mmol potassium chloride (KCl) and 43.9 mmol sodium hydroxide (NaOH) were dissolved in water to form 1 L of aqueous solution;

The prepared buffer solutions and related glass containers were sterilized in 1.03×10^5 Pa and 121 °C for 2 h, then stored in sterile condition.

2.2. Soil

Three types of soil were collected to conduct experiments: black soil (form Harbin, Heilongjiang Province), paddy soil (from Wuxi, Jiangsu Province) and red soil (from Quzhou, Zhejiang Province). The physical and chemical properties of three kinds of soil are listed in Table S1. Fresh soils were passed through a 2 mm sieve for removal of particles and nondecomposed plant residues, and then stored at room temperature for no more than four weeks or 4 °C for less than six months.

2.3. Experimental setup

2.3.1. Preparation of standard solutions

The standard stock solution of 1000 mg/L was prepared in