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Dissipation, occurrence and risk assessment of a phenylurea herbicide tebuthiuron in sugarcane and aquatic ecosystems in South China[☆]



Yuan Qian^{a,1}, Haruna Matsumoto^{a,1}, Xiaoyu Liu^{a,1}, Shuying Li^a, Xiao Liang^b, Yanan Liu^a, Guonian Zhu^a, Mengcen Wang, Ph.D.^{a,*}

^a Institute of Pesticide and Environmental Toxicology, Zhejiang University, Hangzhou 310058, China

^b Environment and Plant Protection Institute, Chinese Academy of Tropical Agriculture Sciences, Haikou 571101, China

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ABSTRACT

In this study, a modified QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) method coupled with UPLC-QqQ-MS/MS analysis was developed to detect tebuthiuron in sugarcane fields and the surrounding aquatic ecosystems. Methodological validation showed the method developed was of favorable sensitivity, reproducibility and accuracy. For assessment of its dietary and ecological risks, dissipation and occurrence of tebuthiuron *in situ* were further investigated through a supervised field trial and an aquatic environment monitoring carried out in six dominant sugarcane production regions in South China. After application at the range of recommended dose, tebuthiuron dominantly distributed in soil, and then dissipated in accordance with the first-order rate model with the half-lives of 12.2–21.5 d. At pre-harvest intervals (PHI), occurrence of tebuthiuron was found to be 0.718–1.366 mg/kg and 0.016–0.034 mg/kg, in sugarcane and soil, respectively. The supervised trials median residue (STMR) of tebuthiuron in sugarcane was thus 0.024 mg/kg and the dietary Risk Quotient (RQ_d) was accordingly calculated as 2.34×10^{-4} , indicating safety on long-term consumption of sugarcane with tebuthiuron residues. Yet high risks of tebuthiuron towards soil ecosystems was noticed as it possessed maximum ecological Risk Quotient (RQ_e) at 1.97 to earthworms. In sugarcane field-surrounding aquatic environment, distribution of tebuthiuron was found to range from 0.007 mg/L to 0.022 mg/L, leading to high risk towards the aquatic ecosystem due to the maximum RQ_e at 440 to algae, irrespective of its low risks to invertebrate and fish. Taken together, our approach serve as an effective tool for monitoring residual tebuthiuron environmentally and also advance in-depth understanding of dietary and ecological risks posed by the phenylurea herbicide.

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1. Introduction

Sugarcane (*Saccharum officinarum*), an important class of economic crops, is mainly cultivated in southern China, especially in Guangxi, Guangdong, Yunnan, and Fujian provinces. As a dominant natural resource of sugar, expanding sugarcane plantation makes China the third largest sugar producer in the world (Li and Yang, 2015). Owing to abundant amino acids, trace elements and a variety of vitamins (Mahmud et al., 2014), sugarcane has been consumed not only as a seasonal fruit and sugar products but also

fresh juice by majority of Chinese people, and it has taken up a large proportion in Chinese dietary consumption with a stable increasing trend since the past decades. However, as cultivation areas of sugarcane rise rapidly, severe suffering from weeds has become a serious challenge to maintenance of yield and quality. According to one previous report, there were exceeding 1000 species of weeds that interfere the balance of sugarcane agro-ecosystems worldwide (Carvalho et al., 2007).

To address this issue, various families of herbicides with broad-spectrum herbicidal activities have been largely applied into sugarcane fields, such as triazine family, sulfonamide family, sulfonylurea family, phenoxyalkanoic acid family, and particularly phenylurea family. Tebuthiuron (1-(5-*tert*-Butyl-1,3,4-thiadiazol-2-yl)-1,3-dimethylurea) belongs to phenylurea herbicide, and has been widely applied to control grassy weeds and broadleaf weeds in most of the sugarcane fields (Fang et al., 2012). As a typical

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* Corresponding author.

E-mail address: wmctz@zju.edu.cn (M. Wang).

¹ Equally contributing authors.

phenylurea herbicide (Caux et al., 1997; du Toit and Sekwadi, 2012; Lane et al., 1997), tebuthiuron is capable of entering the weeds via roots and foliar absorption, and killing the weeds by inhibition of electron transport primarily at the reducing side of photosystem II of photosynthesis (Hatzios et al., 1980; Hussain et al., 2015). Moreover, this herbicide belongs to a non-selective herbicide with a broad spectrum of action against various weeds (du Toit and Sekwadi, 2012).

Owing to the high water solubility and low adsorption to soil particles, (du Toit and Sekwadi, 2012; Helling and Acker, 2005; Mickelson et al., 2001), residual tebuthiuron might enter a wide array of related ecological systems including the groundwater, surrounding aquatic ecosystems and agricultural ecosystems through diverse environmental behaviors (Donald et al., 2004; Kolpin et al., 2000; Mickelson et al., 2001; Siber et al., 2009), leading to environmental contamination and potential hazardous effects on non-target organisms via the food chain bioaccumulation (Donald et al., 2004; Siber et al., 2009). For instance, tebuthiuron appeared to pose a significant and prolonged risk to native freshwater plant species, particularly phytoplankton and floating macrophytes (van Dam et al., 2004). Besides, tebuthiuron exerted cellular toxicity on algae (*Selenastrum capricornutum*) in a chronic study, which was attributed to its inhibition on photosynthesis as it suppressed growth of terrestrial plants (Meyerhoff et al., 1985). These side effects exerted by tebuthiuron are largely dependent on the residual profile in the sugarcane field *in situ*, the most widely applied agricultural environment, but it remained obscure. Besides, the potential risks of agrochemical residue contamination to human beings and environmental organisms were known to be dominantly caused by dietary intake of the agrochemicals-contaminated food (Bouwman et al., 2012) and/or environmental exposure (Tisler et al., 2016), and a variety of relevant risk assessment methodologies have also been developed, particularly the risk quotients (RQs) evaluation (Ccanccapa et al., 2016). In the case of tebuthiuron, the field data-based RQs evaluation was thus considered to be capable of reflecting its dietary and ecological risks.

Effective extraction and sensitive determination play critical roles in monitoring agrochemicals and environmental pollutants. As initially developed in 2003, QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) extraction has been widely applied for extraction and purification of a wide array of compounds from various matrices such as fruit, vegetable and also environmental samples (Inostroza et al., 2016), particularly its salting-out effect is capable of raising recoveries of polar compounds (Hepperle et al., 2015), we thus intended to adopt QuEChERS-based approach for extraction and purification of tebuthiuron. For determination of tebuthiuron, diverse analytical approaches such as gas chromatography (GC) with a nitrogen-phosphorus detector (NPD) (Scott, 1993), high performance liquid chromatography (HPLC) (Ferracini et al., 2005), and gas chromatography with mass spectrometry (GC-MS) (Bahnmann et al., 2007) have been reported. As far as we know, there are no studies devoted to fast and reliable methodology for analysis of residual tebuthiuron in both plant- and environmental origins.

In this work, we initially aim to develop a fast, convenient and reliable analytical method to determine tebuthiuron residues in sugarcane fields and the surrounding aquatic ecosystems. A modified QuEChERS method has been developed for the extraction of tebuthiuron in sugarcane and the related environmental matrices. The subsequent determination has been performed by UPLC-QqQ-MS/MS (ultra performance liquid chromatography-triple quadrupole tandem mass spectrometry). Meanwhile, we selected six dominant sugarcane production regions in South China to carry out field trial and environmental monitoring, for simulation and

tracing of tebuthiuron residues in sugarcane ecosystems and associated aquatic ecosystems. Finally, the developed method has been fully validated and applied to characterization of residual pattern and potential risks of tebuthiuron.

2. Materials and methods

2.1. Chemicals and reagents

Tebuthiuron standard (100 mg/L in methanol, pesticide residue analysis grade) was purchased from J&K Chemicals (China). Tebuthiuron (95%, technical grade) were purchased from Runze Pharmaceutical Suzhou Co., Ltd (China) and prepared as 500 g/L suspension concentrates (SC) for field trial. Methanol (chromatographic grade) and other organic solvent (analytical grade) were purchased from Sigma-Aldrich (USA). Ultrapure water was purified via a Milli-Q Water Purification System (Merck Millipore, Germany). The one-off membrane (0.22- μ m, polytetrafluoroethylene, PTFE) micro-filter (MITEX, Millipore, USA) was used to filter the analyte. DisQuE Kit including centrifuge tube, magnesium sulfate, sodium acetate and primary secondary amine (PSA) was purchased from Waters (USA).

2.2. Extraction and purification

For pre-treatment, the sugarcane and sugarcane leaf were evenly grinded by a food mill, and the soil was dispersed and sieved through a 2 mm-mesh, and the water was filtered through no. 101 filter paper (Advantec, Tokyo, Japan). To extract tebuthiuron from the sugarcane and associated environmental matrixes, the modified QuEChERS technique (Ko et al., 2014) was applied using the DisQuE Kit. The pre-treated sugarcane (10 g), sugarcane leaf (10 g), soil (20 g) and water (20 mL) samples, were respectively weighed into a 250-mL centrifuge bottle and then supplemented with 50 mL ultrapure water (for sugarcane, leaf and soil samples only) and 50 mL acetonitrile. The resulting mixtures were shaken in a thermostatic oscillator (ZHWHY-2102C, ZHICHENG, China) at 180 rpm for 40 min at 30 °C. After centrifugation at 4000 rpm for 5 min, the aliquot of the supernatant (25 mL) was pipetted into a 50-mL DisQuE centrifuge tube preloaded with 6 g magnesium sulfate and 1.5 g sodium acetate. Each mixture was shaken drastically for 1 min and centrifuged at 4000 rpm for 5 min and then the supernatant was concentrated by a rotatory evaporator at 45 °C for further purification (Cao et al., 2015).

The concentrates were re-dissolved with 2 mL of methanol and pipetted into a 2 mL clean-up tube filled with 50 mg PSA and 150 mg magnesium sulfate. After storing under -20 °C for 1 h, the tube was centrifuged at 4000 rpm for 3 min. After filtration through a 0.22- μ m PTFE micro-filter, the filtrates were subjected to quantitative analysis of tebuthiuron using UPLC-QqQ-MS/MS.

2.3. Qualitative and quantitative analysis of tebuthiuron

The tebuthiuron standard in methanol at 100 mg/L was diluted in the matrices at a series of concentration (0.001, 0.005, 0.01, 0.05, 0.1, 1.0 and 10.0 mg/L) to generate working standard solution for quantitative analysis of tebuthiuron in various matrixes (external standard method). All resulting solutions were stored in amber bottles at 4 °C.

For UPLC-QqQ-MS/MS (ultra performance liquid chromatography-triple quadrupole tandem mass spectrometry) qualitative and quantitative analyses, a DIKMA Endeavorsil™ C18 (2.1 mm \times 100 mm, 1.8 μ m, China) column was installed in a Acquity™ Ultra Performance LC coupled with Applied Biosystems SCIEX Triple Quad™ 5500 (Applied Biosystems, USA). Mobile phase

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