Chemosphere 144 (2016) 201–206

Contents lists available at ScienceDirect

Chemosphere

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

Dissipation and distribution of chlorpyrifos in selected vegetables through foliage and root uptake

Jing Ge[a,b,1], Mengxiao Lu[b,1], Donglan Wang[a,b], Zhiyong Zhang[a,b], Xianjin Liu[a], Xiangyang Yu[a,b,*]

[a] Key Laboratory of Food Quality and Safety of Jiangsu Province – State Key Laboratory Breeding Base/Key Laboratory of Control Technology and Standard for Agro-product Safety and Quality, Ministry of Agriculture, Nanjing 210014, China
[b] Institute of Food Quality and Safety, Jiangsu Academy of Agricultural Sciences, 50 Zhongling Street, Nanjing 210014, China

HIGHLIGHTS

- Chlorpyrifos can be transferred both upwards and downwards in pakchoi and lettuce.
- Lettuce roots have higher tolerance to chlorpyrifos.
- Lettuce has greater ability to translocate chlorpyrifos from shoots to roots.
- Pakchoi has greater ability to translocate chlorpyrifos from roots to shoots.

ARTICLE INFO

Article history:
Received 25 June 2015
Received in revised form 18 August 2015
Accepted 24 August 2015
Available online 9 September 2015

Handling editor: Klaus Kümmerer

Keywords:
Chlorpyrifos
Distribution
Uptake
Translocation
Root concentration factor

ABSTRACT

Dissipation, distribution and uptake pathways of chlorpyrifos were investigated in pakchoi (*Brassica chinensis* L.) and lettuce (*Lactuca sativa*) with foliage treatments under a greenhouse trial and root treatments under a hydroponic experiment. The dissipation trends were similar for chlorpyrifos in pakchoi and lettuce with different treatments. More than 94% of chlorpyrifos was degraded in the samples for both of the vegetables 21 days after the foliage treatments. For the root treatment, the dissipation rate of chlorpyrifos in pakchoi and lettuce at the low concentration was greater than 93%, however, for the high concentrations, the dissipation rates were all under 90%. Both shoots and roots of the vegetables were able to absorb chlorpyrifos from the environment and distribute it inside the plants. Root concentration factor (RCF) values at different concentrations with the hydroponic experiment ranged from 5 to 39 for pakchoi, and from 14 to 35 for lettuce. The translocation factor (TF) representing the capability of the vegetables to translocate contaminants was significantly different for pakchoi and lettuce with foliage and root treatments. The values of TF with foliage treatments ranged from 0.003 to 0.22 for pakchoi, and from 0.032 to 1.63 for lettuce. The values of TF with root treatments ranged from 0.01 to 0.17 for pakchoi, and from 0.003 to 0.23 for lettuce. Significant difference of TF was found between pakchoi and lettuce with foliage treatments, and at high concentrations (10 and 50 mg L^{-1}) with root treatments as well. However, there was no significant difference of TF between pakchoi and lettuce at 1 mg L^{-1} with root treatment.

1. Introduction

Chlorpyrifos is a broad-spectrum organophosphorous insecticide widely used throughout the world in agricultural and urban pest control (Giddings et al., 1997). It has limited solubility in water (approximately 1.3 mg L^{-1}) and moderately high log ^{kow} (the logarithm of octanol/water partition coefficient). As a hydrophobic compound, it is preferential for chlorpyrifos to partition from water to surfaces, like soil and plants (Rogers and Stringfellow, 2009). Chlorpyrifos has short to moderate persistence in the environment as a result of several pathways of dissipation, including volatilization, photolysis, microbial degradation etc (Williams et al., 2014). However, the massive use of chlorpyrifos has still increased public concerns on food and environment safety. It has been reported that exposure to chlorpyrifos can cause the alteration of polyamine metabolism and embryonic malformations for *Rhinella arenarum* (Sotomayor et al., 2012), and also induce oxidative stress and DNA damage (Gupta et al., 2010; Khalil, 2015).

The environmental fate of chlorpyrifos has been extensively studied. Kuhr and Tashiro (1978) studied the distribution and per-

* Corresponding author. Institute of Food Quality and Safety, Jiangsu Academy of Agricultural Sciences, 50 Zhongling Street, Nanjing 210014, China.
E-mail address: yuxy@jaas.ac.cn (X. Yu).
[1] These authors contributed equally to this work and should be considered as co-first authors.

http://dx.doi.org/10.1016/j.chemosphere.2015.08.072
0045-6535/

sistence of chlorpyrifos applied to turf. In the study, liquid and granule formulations were investigated and the results showed that more chlorpyrifos reached the soil when formulated as a granule. Racke et al. (1994) studied the dissipation of chlorpyrifos in five different soils at termiticidal application. The degradation of chlorpyrifos was mainly affected by the initial concentrations and the temperature. Zhang et al. (2012) studied the dissipation of chlorpyrifos in rice, soil and water under paddy field conditions. Partitioning of chlorpyrifos to soil and plants in vegetated agricultural drainage ditches was studied by Rogers and Stringfellow (2009), and absorption of chlorpyrifos to whole plant stems was more than 10 times higher than that to soil, indicating plants as a preferential media for chlorpyrifos to partition to.

However, little attention has been given to compare the uptake and translocation of chlorpyrifos in vegetables through foliage and root treatments. The main purpose of this study was to investigate the distribution and uptake of chlorpyrifos in two commonly consumed vegetables pakchoi and lettuce under greenhouse trial with foliage treatment and laboratory hydroponics with root treatment. Hopefully the results could fill the gap of uptake and translocation behavior of chlorpyrifos in vegetables and also be used for further evaluation of the effect of different treatments and different cultivation systems on the uptake of chlorpyrifos in vegetable farming systems.

2. Materials and methods

2.1. Reagents and materials

Test pesticide: Chlorpyrifos standard was from Dr. Ehrenstorfer (Germany), and 40% chlorpyrifos EC was purchased from Hubei Xianlong Chemical Industry Co., Ltd. (Hubei, China).

Reagents: Acetone, acetonitrile and n-hexane (A.R.) were obtained from Shanghai Pilot Chemical Corporation (Shanghai, China). Florisil of 60–100 mesh (Supulco Inc., USA) was activated at 450 °C for 4 h. Anhydrous sodium sulfate (Xilong Chemical Co., Ltd., China) was baked at 450 °C for 4 h. Sodium Chloride (NaCl), calcium nitrate tetrahydrate ($Ca(NO_3)_2{\cdot}4H_2O$), potassium nitrate (KNO_3), ammonium nitrate (NH_4NO_3), monopotassium phosphate (KH_2PO_4), magnesium sulfate heptahydrate ($MgSO_4{\cdot}7H_2O$), ferrous sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$), ethylenediamine tetraacetic acid disodium (EDTA-2Na), potassium iodide (KI), manganese sulfate ($MnSO_4$), zinc sulfate ($ZnSO_4$), sodium molybdate (Na_2MoO_4), cobalt chloride ($CoCl_2$), sodium hydroxide (NaOH) and hydrochloric acid (HCl) were all purchased from Xilong Chemical Co., Ltd. Boronic acid (H_3BO_3) and copper sulfate ($CuSO_4$) were obtained from Kemi'ou Chemical Reagent Co. Ltd. (Tianjin, China).

2.2. Greenhouse trial and laboratory hydroponic experiment

A greenhouse trial and a hydroponics experiment were designed to evaluate the distribution and uptake of chlorpyrifos through shoots and roots of the vegetables, respectively.

Greenhouse trial: The field trial was carried out in a greenhouse at the experiment station (Lishui, Jiangsu province) of Jiangsu Agricultural Academy of Sciences. The soil type in this area was yellow brown soil. The pH of the soil was 5.9–6.4 and the content of organic matter was 21–25 g/kg. Pakchoi (*Brassica chinensis* L.) and lettuce (*Lactuca sativa*) were cultivated in the greenhouse at the experiment station in September 2013. Three replicates of the plots for each vegetable were set up with a buffer area of 0.5 m^2 between each two plots. Forty percent chlorpyrifos EC was applied to the vegetables on October 21st 2013, a.i. 0.097 g/m^2. The leaves of the vegetables were all overlapped and covered approximate 95% of the growing region when the pesticide was applied. Plant and soil samples were randomly collected from each plot at 2 h, 1, 3, 5, 7, 10, 14, 21 d after application. The blank samples were collected before applying chlorpyrifos.

Laboratory hydroponic experiment: Hydroponic experiment was carried out in the laboratory of Jiangsu Agricultural Academy of Sciences. The vegetables were grown in cans first and then transplanted into plastic containers with a nutrient solution. Each container was planted with 10 plants. The nutrient solution modified from Hoagland's nutrient solution formula was added accordingly during the vegetable growing period. The composition of the culture medium was: KNO_3 (506 mg L^{-1}), KH_2PO_4 (136 mg L^{-1}), $MgSO_4$ (493 mg L^{-1}), NH_4NO_3 (80 mg L^{-1}), $Ca(NO_3)_2.4H_2O$ (945 mg L^{-1}), ferric salt solution (2.5 mL, pH 5.5) and trace element solution (5 mL, pH 6.0). The ferric salt solution contained 2.78 g $FeSO_4{\cdot}7H_2O$, 3.73 g EDTA-2Na and 500 mL of deionized water. The trace element solution contained 0.83 mL of KI, 6.20 mg L^{-1} of H_3BO_3, 22.30 mg L^{-1} of $MnSO_4$, 8.60 mg L^{-1} of ZnSO4, 0.25 mg L^{-1} of Na_2MoO_4, 0.025 mg L^{-1} of $CuSO_4$, 0.025 mg L^{-1} of $CoCl_2$.

The vegetables were transplanted to the nutrient solution containing different levels of chlorpyrifos at 1 mg L^{-1}, 10 mg L^{-1} and 50 mg L^{-1}. Each container contained 1.5 L of the nutrient solution and the level of the solution was marked. A group of nine containers for each level of chlorpyrifos was set for the experiment and each container was planted with 10 plants. The control groups included the nutrient solution with vegetables and the nutrient solution without vegetables but with the same levels of chlorpyrifos as the experimental group. After 5-day exposure, the contaminated vegetables were transferred to the blank nutrient solutions to grow. Shoots, roots and blank solution samples were collected at 2 h, 1, 2, 3, 5, 7, 10, 14 and 21 d after the transfer.

Roots and shoots of the vegetables were separated and chopped into small pieces. All the samples were stored at −20 °C until analysis.

2.3. Extraction, clean up and analysis

Shoots: Shoot samples were homogenized with a blender. An aliquot of 5.0 g shoot sample was extracted with 10 mL of acetonitrile. After vortexing for 1 min and homogenizing for 2 min, 2.0 g NaCl was added to the mixture and then vortex for another min. After centrifugation for 5 min at 5000 r/min, 1 mL of supernatant was dried under a gentle nitrogen gas stream and redissolved in n-hexane for cleanup. The extract was subjected to florisil cleanup with the procedure as follows: A mass of 0.5 g florisil was placed into a 0.5 cm diameter glass pipettes with frit at the bottom. The column was sequentially conditioned with 5 mL of hexane: acetone (90:10) and 5 mL of hexane. The sample extract was loaded on the top of the column, and the eluent was collected with a 10-mL test tube. The tube contained the sample extract was rinsed with 5 mL of hexane: acetone (90:10) and the solution was loaded on the top of the column. The eluent was collected into the same 10-mL test tube. The eluent was dried under a gentle nitrogen stream and dissolved in 1 mL of acetone. Then the extract was filtered through a 0.22-μm membrane into a sample vial for GC-ECD analysis.

Roots: Root samples were cut into fine pieces. An aliquot of 1.0 g root sample was extracted with 5 mL of acetone. After vortexing for 1 min and homogenizing for 2 min, 2.0 g NaCl was added to the mixture then vortex for another min. After centrifugation for 5 min at 5000 r/min, 1 mL of supernatant was dried under a gentle nitrogen gas stream and dissolved in 1 mL of acetone. Then the extract was filtered through a 0.22-μm membrane into a sample vial for GC-ECD analysis.

Soil: An aliquot of 5.0 g soil sample was mixed with 5 g NaCl and extracted with 20 mL of acetonitrile. The mixture was vortexed for 1 min, extracted with ultrasound for 30 min and shaken with