Chemosphere 180 (2017) 42–47

Contents lists available at ScienceDirect

Chemosphere

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

Pesticide residues in nut-planted soils of China and their relationship between nut/soil

Yongxiang Han [a, 1], Runhong Mo [a, 1], Xinyue Yuan [b], Donglian Zhong [a], Fubin Tang [a], Caifen Ye [a], Yihua Liu [a, *]

[a] Research Institute of Subtropical Forestry, Chinese Academy of Forestry, Fuyang 311400, China
[b] Testing Center for Food Safety of Fuyang District of Hangzhou, Fuyang 311400, China

HIGHLIGHTS

- Multiple residues (up to 14) were found in 76.3% nut-planted soils.
- 15 pesticides were found in the nut-planted soils, and triadimefon was the most frequently detected pesticide.
- A significant correlation between pesticide residues in nuts and soils was observed (r = 0.83).
- Some pesticides could accumulate in nut by the uptake effect from soil.

ARTICLE INFO

Article history:
Received 19 December 2016
Received in revised form
30 March 2017
Accepted 31 March 2017
Available online 4 April 2017

Handling Editor: I. Cousins

Keywords:
Nut
Soil
Pesticide residue
Relationship

ABSTRACT

Twenty-nine pesticide residues in nut-planted soils from China were investigated. One organophosphate (chlorpyrifos) was detected in 5.3% soils, and the residue levels of 7.2 μg/kg to 77.2 μg/kg. The concentrations of six organochlorines (DDT, HCH, endosulfan, quintozene, aldrin and dieldrin) detected in 78.9% soils were 0.6 μg/kg to 90.1 μg/kg. The residue levels of six pyrethroids (bifenthrin, fenpropathrin, cyhalothrin, cypermethrin, fenvalerate and deltamethrin) detected in 65.8% soils were 1.5 μg/kg to 884.3 μg/kg. Triadimefon and buprofezin were found in 71.1% and 52.6% samples, respectively, with the corresponding concentrations of 9.8 μg/kg to 193.7 μg/kg and 87.9 μg/kg to 807.4 μg/kg. The multiple residues were found in 76.3% soils. A significant correlation between pesticide residues in nuts and soils was observed, with the correlation coefficient (r) 0.83 ($P < 0.001$). In addition, the bioconcentration factor (BCF) values for the explanation of pesticides from soils into nuts were ranged from 0.8 to 16.5. The results showed that some pesticides could accumulate in nut by the uptake effect from soil.

1. Introduction

A large number of chemical pesticides have been applied in agriculture. Although pesticides reduce crop yield losses and improve food quality, they are inherently toxic to living organisms and likely to have negative impacts on human health via exposure to residues in food commodity (Liu et al., 2016a). Nowadays, maximum residues limits (MRLs) and monitoring project for agricultural products were built in many countries in order to control the quantity of pesticide in food (Skretteberg et al., 2015). Pesticides were found in 27.3% of fruit, vegetables, cereals, herbs and seeds samples in Poland (Szpyrka, 2015). The levels of pesticide concentrations in various vegetables (Li et al., 2014) and fruits (Liu et al., 2016b) collected from China were reported. However, compared with these foods, there were few reports regarding of pesticide residues in the planted soils for food production.

Since most of the crops planted in the soil, the soil has an extremely important effect on the crop pesticide residues. Most of the previous papers focused on the detection of organochlorine pesticides in the different soils, due to their persistence in the environment. The detection frequencies for DDTs, α-HCH and β-HCH in the soils from Midway Atoll (North Pacific Ocean) were 98%, 95% and 84%, respectively (Ge et al., 2013). Five insecticides residues (chlorpyrifos, malathion, proenofos, triazophos and cypermethrin) were found in the soil samples from 11 out of 26 farms located in Sta. Maria of Pangasinan (Del Prado-Lu, 2015). The total

* Corresponding author.
E-mail address: liuyh@caf.ac.cn (Y. Liu).
[1] Co-first author.

http://dx.doi.org/10.1016/j.chemosphere.2017.03.138
0045-6535/

organochlorine pesticides concentrations ranged from 31 to 365 ng/g in soil samples (n = 28) collected from Gujranwala division, Punjab Province, Pakistan (Mahmood et al., 2014). The concentrations of chlorpyrifos in the vegetable soil samples (collected from coastal areas in Togo) varied from non-detectable to 26.93 μg/kg. The reports focusing on pesticides were less for nuts than those in fruits and vegetables (Liu et al., 2016a), especially for nut-planted soil. It is widely known that nuts are a rich source of nutrients and have potential health benefits. In recent years, the nut production of China had a rapid development, and a large number of products exported to the United States, the European Union and other countries every year. To the best of our knowledge, there is no information available about the pesticide residues in the nut-planted regions of China. One of the objectives of this study was to find the answer for this matter.

Many previous works suggested that there were some relationship of pesticide residues among the plants, fruits and their soils. Pesticide residues in soil were mainly from direct application and some pesticides could be stable in the environment. Twelve hours after the foliar application, the concentrations of cypermethrin in soils from sunflower cultivated plots were ranged from 0.009 to 0.015 μg/g (Mantzos et al., 2016). Besides the direct application, the uptake effect (from soil into plant) plays an important role for pesticide detection in crops. The uptake of endosulfan from soil onto the sunflower was reached to top at its cultivation of 60 days, with the highest pesticide levels in roots (>4000 μg/kg) and leaves (>200 μg/kg) (Mitton et al., 2016). The uptake effect is especially important for some persistent pesticides (such as DDT and HCH), which had a large-scale usage history. Although they have been banned for a long time, they are still detected in plants (Wang et al., 2016a), water (Lu and Liu, 2016) and soils (Wang et al., 2016b). Their detections were mainly caused by plant uptake effect or bioconcentration. Some mathematical models were even built to predict the uptake effect (Ding et al., 2014; Trapp, 2007). Considering the biomass production and accumulation potential, sunflower could accumulate more endosulfan from soils than other crops did (Mitton et al., 2016). There were some reports about different pollutants (pesticides, heavy metals, toxin) (Pandey et al., 2010; Schneider et al., 2014; Palumbo et al., 2015) detection in nuts. Another work reported different pesticide residues in California almond and almond-planted soils and to evaluate the risk for environment and human health (Liu et al., 2012; Zhan and Zhang, 2014). However, more information about the pesticide residues in nuts and soils should be investigated. Moreover, the pervious reports about the relationship of pesticide residues between foods and soils were focused on various vegetables, few of them considered the tree-fruits. To be our knowledge, there had none of any report about the relationship between nuts and their produced soils. In the previous study (Liu et al., 2016a), we have investigated the pesticides concentrations in three kinds of nuts. Another objective of this study was to investigate if there was any uptake effect between the nuts and their soils.

2. Materials and methods

2.1. Chemicals

All the pesticide analytical standards were purchased from the National Information Center for Certified Reference Materials (Beijing, China). Analytical standards of ≥98% purity were used. Acetone and hexane (GC-grade) were obtained from Merck (Darmstadt, Germany). Other solvents (analytical purity) were from Shanghai Guo Yao Chemical Reagents (Shanghai, China). ASE-12 solid-phase extraction and nitrogen evaporators MTN-5800 were obtained from Auto Science Company (Tianjin, China).

2.2. Sample collection

During the nut harvest season (2013–2014), thirty-eight nut soils (depth of 20 cm) were collected from the main producing areas of China (seven province: Heilongjiang, Jilin, Hebei, Hubei, Sichuan, Jiangxi, Yunnan). The details for the sampling locations and collection procedures could be seen in our previous paper (Liu et al., 2016b). All samples were stored at −20 °C until analysis.

2.3. Sample extraction, cleanup and analysis

5.0 g of soil sample (sieved by 2 mm mesh) was extracted by methanol and acetone (1:1, v/v). The extracts could be directly analyzed for organophosphates (OPs). However, the samples should be purified by fiorisil SPE before the analysis of organochlorines (OCs) and pyrethroids (PYs). The samples were finally analyzed by GC with FPD and ECD detector. The external standard calibration curve method was used for the data computing. Details about the analysis procedure could be seen in the previous work (Liu et al., 2016b).

2.4. Statistical analysis

Data were analyzed by SPSS base 17.0 software. ANOVA (followed by least significant difference test) was used to determine the differences among means.

3. Results and discussion

3.1. The levels of organophosphates (OPs) in soils

The levels of OPs in the collected soil samples are shown in Table 1. Chlorpyrifos was the only pesticide detected in two soil samples, with the detected concentrations 7.2 μg/kg in one chestnut soil sample and 77.2 μg/kg in one pinenut soil sample, respectively. The results were similar with our previous work for persimmon and jujube soils, in which chlorpyrifos was one of the two detected OPs (another was dimethoate) and the detected concentrations ranged from 8.8 μg/kg–25.5 μg/kg (Liu et al., 2016b). During the samples (persimmon/jujube/nut soils) collection, we learned from the local farmers that chlorpyrifos was the most frequently used OPs in these areas in recent years. The degradation half-life of chlorpyrifos in soil depends on the soil type and climate, and its ranged from several days to more than 100 days (Liu et al., 2014), respectively. Thus, it was not surprising that chlorpyrifos could be detected in persimmon/jujube soils and the

Table 1
The levels of organophosphates in the tested nut soils (μg/kg).

Pesticide	Chestnut soil	Walnut soil	Pinenut soil	LOD
Dichlorvos	n.d.	n.d.	n.d.	10
Methamidophos	n.d.	n.d.	n.d.	10
Acephate	n.d.	n.d.	n.d.	10
Phorate	n.d.	n.d.	n.d.	10
Omethoate	n.d.	n.d.	n.d.	50
Dimethoate	n.d.	n.d.	n.d.	10
Chlorpyrifos	n.d.-7.2	n.d.	n.d.-77.2	5
Parathion-methyl	n.d.	n.d.	n.d.	5
Fenthion	n.d.	n.d.	n.d.	10
Fenitrothion	n.d.	n.d.	n.d.	10
Parathion	n.d.	n.d.	n.d.	5
Isocarbophos	n.d.	n.d.	n.d.	10
Phosmet	n.d.	n.d.	n.d.	10
Monocrotophos	n.d.	n.d.	n.d.	10
Triazophos	n.d.	n.d.	n.d.	10

n.d. = not detectable.