Science of the Total Environment 542 (2016) 620–628

Contents lists available at ScienceDirect

Science of the Total Environment

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

Pesticides in persimmons, jujubes and soil from China: Residue levels, risk assessment and relationship between fruits and soils

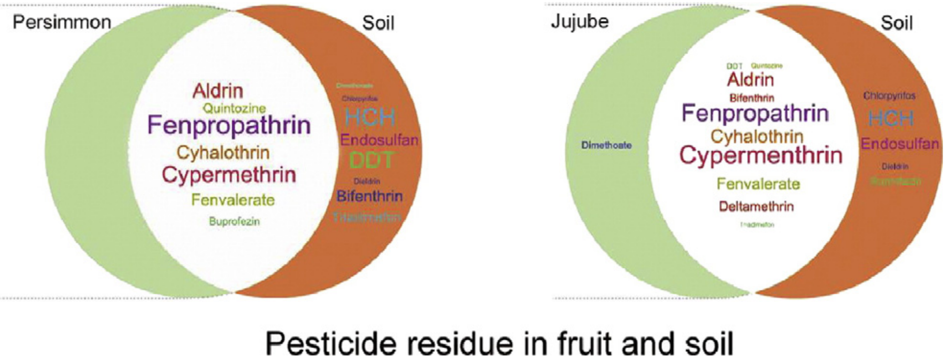
Yihua Liu, Shiliang Li, Zhanglin Ni, Minghua Qu, Donglian Zhong, Caifen Ye, Fubin Tang *

Research Institute of Subtropical Forestry, Chinese Academy of Forestry, Fuyang 311400, China

HIGHLIGHTS

- 36.4% of persimmon and 70.8% of jujube samples contain pesticide residues;
- 4.5% (persimmon) and 25.0% (jujube) samples exceeded the MRLs set by China;
- consumption risk from cyhalothrin, aldrin and dieldrin give cause for concern.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 27 August 2015
Received in revised form 27 October 2015
Accepted 28 October 2015
Available online 3 November 2015

Editor: A Covaci

Keywords:
Persimmon
Jujube
Soil
Pesticide
Residue
Risk assessment

ABSTRACT

Extreme and uncontrolled usage of pesticides produces a number of problems for vegetation and human health. In this study, the existence of organophosphates (OPs), organochlorines (OCs), pyrethroids (PYs) and fungicides (FUs) were investigated in persimmons/jujubes and their planted soils, which were collected from China. One OP (dimethoate), three OCs (DDT, quintozene and aldrin), six PYs (bifenthrin, fenpropathrin, cyhalothrin, cypermethrin, fenvalerate and deltamethrin) and two FUs (triadimefon and buprofezin) were found in 36.4% of persimmons and 70.8% of jujubes, with concentrations from 1.0 μg/kg to 2945.0 μg/kg. The most frequently detected pesticides in the two fruits were fenpropathrin in persimmons and cypermethrin in jujubes, with the detection frequencies of 30.0% and 22.7%, respectively. The residues of 4.5% (persimmon) and 25.0% (jujube) of samples were higher than the maximum residue limits (MRLs) of China. Compared with the fruits, more types of pesticides and higher residues were observed in their planted soils. The most frequently detected pesticides were HCH in persimmon soil and DDT in jujube soil, with the detection frequencies of 10.9% and 12.7%, respectively. For the tested samples, 39.1% of fruit samples and 63.0% of soil samples with multiple residues (containing more than two pesticides) were noted, even up to 8 residues in fruits and 14 residues in soils. Except for cyhalothrin, the other short-term risks for the tested pesticides in the fruits were below 10%, and the highest long-term risk was 14.13% for aldrin and dieldrin. There was no significant health risk for consumers via consumption of the two fruits.

Abbreviations: OPs, organophosphates; OCs, organochlorines; PYs, pyrethroids; FUs, fungicides; GC, gas chromatography; LOD, limit of detection; LOQ, limit of quantification; MRL, maximum residue limit; aHI, acute/short-term consumer health risk; ESTI, estimated short-term intake; ARfD, acute reference dose; HQ, chronic/long-term consumer health risk; EDI, estimated daily intake; ADI, acceptable daily intake; cHI, cumulative risk.

* Corresponding author.
E-mail address: yalin_zj@163.com (F. Tang).

http://dx.doi.org/10.1016/j.scitotenv.2015.10.148

1. Introduction

The use of pesticides for crop protection is expected to increase based on a growing world population and the need for more food supplies. While pesticides increase agricultural production, bioaccumulation through the food chain can eventually become a risk to mammals because the pesticides induce certain negative effects. Public health concerns regarding the improper use of pesticides and poison have increased in recent years. To date, certain countries, regions and international organizations have established maximum residue limits (MRLs) for foodstuffs. Additionally, national food monitoring programs for pesticides have been enacted worldwide (Jardim and Caldas, 2012; Lozowicka et al., 2014; Skretteberg et al., 2015) to ensure consumer health, improve management of agricultural resources and prevent economic losses.

There have been numerous reports regarding pesticide residues detected in grains (Lozowicka et al., 2014), vegetables (Shoiful et al., 2013), milk (Tsakiris et al., 2015) and fish (Wu et al., 2013). Fruits are one of the most important foodstuffs in people's diets, and several reports also focused on their pesticide levels. In a Nordic project on pesticide residues in fruit and vegetables imported from Southeast Asia, 12% of the samples exceeded the EU MRLs (Skretteberg et al., 2015). Pesticides were found in over 60% of apple samples in Poland, and the most frequently detected pesticides were fungicides (Lozowicka, 2015). At least one pesticide was detected in 70.5% of the tomato samples from Bogota, Colombia, and the most detected pesticides were pyrimethanil, carbendazim, dimethomorph and acephate (Arias et al., 2014). However, information regarding pesticide residue levels in persimmons (*Diospyros* spp.) and jujubes (*Ziziphus* spp.) are scarce. Persimmons and jujubes are important fruit commodities, and they could be made into various dry fruits and jams. There are several reports regarding pesticide residue in persimmons and jujubes. The determination of pesticide residues in persimmons using gas chromatography/negative chemical ionization-mass spectrometry (GC/NCI-MS) (Barreda et al., 2006) and liquid chromatography–tandem mass spectrometry (LC–MS) (Min et al., 2011) and in jujubes using gas chromatography and mass spectrometry (GC–MS) (Zhao et al., 2014) has been developed. After two, three or four applications, pyrimethanil residues on the collected persimmons averaged 0.44, 0.48 or 0.53 mg/kg, respectively (Shim et al., 2007). The pesticide residues of persimmons were only reported on samples collected from Konya (Ucan et al., 2009), Brazil (Ciscato et al., 2009) and Pakistan (Parveen et al., 2011). The presence of pesticide residues in jujubes has not been determined in any countries. China ranks 1st in the world for persimmon and jujube production, and many products are exported to other countries every year. One of the aims of the present study was to determine the concentrations of pesticides (organophosphate, organochlorine, pyrethroid and 2 fungicides) in persimmons and jujubes collected from different main producing regions of China between 2013 and 2014, as well as to evaluate the health effects of detected residues.

Soil plays an important role in the pesticide residue in plants. There are two pathways for pesticide transfer between the plants and their planted soils. Firstly, most of the pesticides could shift or fall onto the soil when the pesticide is applied onto plants. Next, most of the deposited pesticide on the plant could be washed off by rainfall to the soil. Secondly, the residues of adsorbed pesticides in soil, especially for organochlorine pollutants, remain as contaminants in the environment because of their long-term persistence and mobility, and they could enter into food again via the plant uptake effect (Fantke and Jolliet, 2015; Fantke et al., 2013). The uptake of contaminants by vegetables has been shown to vary with vegetable types. There were significant positive correlations between the polychlorinated biphenyls (PCBs) and organochlorine pesticide (OC) concentrations ($p < 0.05$) in soils and organic-farmed carrots but no significant correlation was found between the concentrations of any contaminants in soils and organic-farmed potatoes (Zohair et al., 2006). Root vegetables accumulate weathered organochlorine pollutants to a greater extent than other vegetables (Florence et al., 2015). In addition, the uptake of contaminants by vegetables has also been shown to vary with soil type, contaminant concentration and contaminant source (Gaw et al., 2008). Some scientists even developed various mathematical models to predict uptake of organic chemicals from soil into plants (Ding et al., 2014; Trapp, 2007), which were validated by field data from apple (Trapp, 2007), radish (Trapp, 2015) and urban afforestation tree species (Ding et al., 2014). However, more information regarding the uptake effect for fruits, especially for tree-planted fruits, should be given. Another aim of this study was to elucidate the relationship of pesticide residues between fruits and their planted soils, especially to determine if the contaminants in the planted soils were available for uptake by persimmons/jujubes and, if so, to establish the relationship between the fruits and soil contaminant concentrations. Among the tested pesticides (Table 1), most OPs and OCs have long been banned for use; however, their long persistence in the environment and/or high toxicity to humans/animals lead to the demand for monitoring their residues in food and the environment. Moreover, the tested pyrethroids and fungicides are the primary pesticides used in persimmon/jujube farming in China.

2. Materials and methods

2.1. Chemicals

Pesticide analytical standards were purchased from the National Information Center for Certified Reference Materials (Beijing, China) with certified quality. Individual pesticide stock solutions (100 mg/L) were prepared in acetone and stored at −20 °C. A series of dilutions containing the mixture of standards was prepared (10 mg/L) in acetone or hexane. GC-grade acetone and hexane were obtained from Merck (Darmstadt, Germany). A Milli-Q-Plus ultrapure water system from Millipore (Milford, MA, USA) was used throughout the study to obtain the HPLC-grade water for the analyses. Other solvents were from Shanghai GuoYao Chemical Reagents (Shanghai, China), with pesticide residue analysis quality.

2.2. Sample extraction and cleanup

2.2.1. Persimmon/jujube sample preparation

A representative portion of the sample (without the kernel) was prepared using a knife and mixed thoroughly using a food chopper. Next, 25.0 g of the homogenized sample mixed with 50 mL of acetonitrile was blended in a homogenizer for 2 min at high speed. The extraction solvent was filtered into a 100 mL graduated measuring cylinder containing 7 g of sodium chloride and then was shaken vigorously with a cap on for at least 1 min; the extraction was allowed to be separated for approximately 10 min, then 25 mL of acetonitrile phase was measured into a 100 mL flask and evaporated to near dryness with a rotary vacuum evaporator at 40 °C. Finally, the extract was reconstituted to 2 mL with acetone for the analysis of organophosphate (OP) residues.

For the analysis of organochlorines (OCs), pyrethroids (PYs) and fungicides (FUs), a purification step was needed as the follows: 10 mL of acetonitrile phase was measured in a 50 mL flask and evaporated to near dryness with a rotary vacuum evaporator at 40 °C. The extract was reconstituted to 2 mL with hexane, loaded into a florisil SPE cartridge (1.0 g, preconditioned with 5 mL of 10% acetone/hexane followed by 5 mL of hexane). The cartridge was eluted using 5 mL of 10% acetone/hexane. The eluant was collected and then evaporated to near dryness with a rotary vacuum evaporator at 40 °C. Finally, the eluant was reconstituted to the final volume of 2.0 mL with hexane.

2.2.2. Soil sample preparation

5.0 g of soil sample (sieved through a 2 mm mesh) was mixed with 2 mL of distilled water for 5 min. The sample was added with 20 mL of