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Evaluation of nine pesticide residues in three minor tropical fruits from southern China

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ABSTRACT

The residue levels of nine pesticides (imidacloprid, acetamiprid, carbendazim, diflubenzuron, chlorbenzuron, phoxim, pyrimethanil, abamectin and iprodione) in 117 samples of three minor tropical fruits (starfruits, wax apples and Indian jujubes) from Hainan, Fujian, Guangdong and Guangxi provinces in China were analyzed using ultra-high performance liquid chromatography tandem mass spectrometry (UPLC-MS/MS) after multi-residue extraction procedures. A total of 78 (66.7%) samples were positive, with residues above the limit of quantification. Indian jujube was the fruit with the highest percentage of positive samples (81.6%), followed by starfruit (61.0%) and finally wax apple (57.9%). Carbendazim was the most frequently detected residue found in 51 (43.6%) samples in the concentration ranges of 34.0–443.8 μg/kg. Diflubenzuron, phoxim, pyrimethanil and abamectin were not detected in any sample. Twenty-nine (24.8%) samples were contaminated with multiple pesticide residues, and the simultaneous occurrence of three different residues was found in one wax apple and two starfruit samples. Estimation of the potential health risks associated with the exposure to the analyzed pesticides was carried out and the estimated daily intakes (EDIs) were very low, ranging from 0.020% of the acceptable daily intakes (ADIs) for chlorbenzuron to 1.13% for carbendazim. These results indicate that despite a high occurrence of pesticides in starfruit, wax apple and Indian jujube, the contamination levels do not contribute significantly to pesticide intakes and are unlikely to have public health effects. Nevertheless, measures should be taken to hasten the registration of pesticides for use on minor fruit crops. The findings also indicate that routine monitoring of pesticide residues in minor fruits is necessary to prevent, control and reduce pesticide contamination and to minimize health risks.

1. Introduction

Minor fruits play an important role in tropical horticulture and have high commercial value in domestic and international markets. Pesticides are widely used in minor fruit crops production and post-harvest handling to control organisms that may spoil the fruits (Botero-Coy, Marín, Ibáñez, Sancho, & Hernández, 2012; Nair, Mathew, Beevi, George, & Rajith, 2013). To date, however, few pesticides have been registered for use on minor tropical fruit crops (Baron, Holm, Kunkel Schwartz, & Markle, 2013; Liu, Xie, Zhang, Cao, & Pei, 2013). These fruit crops are grown in such small amounts and therefore it is a minor market for pesticides and the costs involved in obtaining research data for pesticides registration are not recouped from the market (International Union of Pure and Applied Chemistry [IUPAC], 2010; Muller, 2007; Song, Shan, Pan, Xu, & Wang, 2010). Thus, registration of pesticides for use on the minor fruit crops has not drawn enough interest from pesticide manufacturers. Because of the lack of legal pesticide options, farmers may retort to the use of un-registered pesticides to protect their crops from destroying by insects or pathogens, particularly in some developing countries (Ciscato, Gebara, & Monteiro, 2009; Jardim & Caldas, 2012).

Minor tropical fruits are currently receiving increased attention because of their unique flavors and functions. To reduce the need for plant protection residues trials for these crops, the grouping of minor tropical fruits and establishing maximum residue limits (MRLs) for pesticide residues in these commodities by

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extrapolations are being developed (Baron et al., 2013). Furthermore, pesticide residues monitoring programs are being implemented in many countries, including the United states (Hjorth et al., 2011), Brazil (Jardim & Caldas, 2012), Spain (Berrada et al., 2010), China (Chen, & Jiao. 2007), Egypt (Dogheim, El-Marsafy, Salama, Gadalla, & Nabil, 2002), India (Kumari, Madan, & Kathpal, 2006; Nair et al., 2013) and Ghana (Bempah, Buah-Kwofie, Denutsui, Asomaning, & Tutu, 2011). These programs are effective tools to ensure minimal pesticide residues in fruits and a high quality of these commodities.

Starfruit (*Averrhoa carambola* L.), wax apple (*Syzygium samarangenese* Merr. & Perry) and Indian jujube (*Zizyphus mauritiana* Lam.) are tropical fruit crops widely grown in South China. Although the annual production levels of these fruits are low, the crops provide both important income resources of livelihood for local residents and essential nutrients in tropical regions of China. In pesticide terminology, *A. carambola* L., *S. samarangenese* Merr. & Perry and *Z. mauritiana* Lam. are all minor tropical fruit crops. To date the pesticide residues in these three fruits haven't been reported. The objective of this research was to investigate the occurrence of nine pesticide residues, as well as their associated risks, in minor fruit samples of starfruit, wax apple and Indian jujube. The nine pesticides were selected in present work because they are widely used in tropical crops belonging to different classes: imidacloprid and acetamiprid (chloronicotinoid insecticide), carbendazim (benzimidazole fungicide), diflubenzuron and chlorbenzuron (benzoylurea insecticide, insect growth regulator), phoxim (organophosphorus insecticide), pyrimethanil (anilinopyrimidine fungicide), abamectin (macrocyclic lactone insecticide and nematicide) and iprodione (dicarboximide fungicide). The results from monitoring of these pesticide residues offer insights for the design of future governmental pesticides control and risk management programs.

2. Materials and methods

2.1. Chemicals and reagents

Individual standard solutions of imidacloprid, acetamiprid, carbendazim, diflubenzuron, chlorbenzuron, phoxim, pyrimethanil, abamectin and iprodione (1 mg/mL in acetonitrile for each pesticide, except carbendazim at 0.5 mg/mL in ethanol) were purchased from the Environmental Quality Supervision and Testing Center, Ministry of Agriculture, Tianjin, China. High performance liquid chromatography (HPLC) grade acetonitrile, methanol and dichlorolmethane were obtained from Fisher Scientific (USA). Analytical pure ammonium acetate (CH_3COONH_4) and NaCl were purchased from the Beijing Reagent Company (Beijing, China). Deionized water (18.2 MΩ cm resistivity) was prepared using the Milli-Q® Integral Water Purification system (Millipore Corporation, USA). For filtration of the extracts, 0.22-μm polytetrafluoroethylene (PTFE) filters were obtained from ANPEL Scientific Instrument Co., Ltd. (Shanghai, China). The NH_2 solid phase extraction (SPE) cartridges (500 mg, 6 mL) were obtained from CNW Technologies GmbH (Germany).

Individual stock standard solutions of the pesticides were prepared at 100 μg/mL using acetonitrile in a flask to dilute 1 mL of each standard solution to 10 mL for imidacloprid, acetamiprid, phoxim, pyrimethanil and abamectin, and to 5 mL for carbendazim. All stock standard solutions were stable for more than 6 months when stored at −20 °C in the dark. Mixed stock standard solutions were prepared in acetonitrile at 10 μg/mL for imidacloprid, acetamiprid, carbendazim, phoxim, pyrimethanil and abamectin, 50 μg/mL for diflubenzuron and chlorbenzuron, and 100 μg/mL for iprodione. Mixed working standard solutions at various concentrations were prepared daily through appropriate dilution of aliquots of the stock solutions in methanol/water (60/40 v/v). Matrix-matched calibration solutions at various concentrations were prepared daily through appropriate dilution of aliquots of the stock solutions in blank matrix extracts after sample SPE clean-up and redissolution procedures.

2.2. Sample preparation

A total of 117 minor tropical fruit samples were collected from six cities (Haikou, Sanya, Nanning, Qinzhou, Zhangzhou and Jieyang) in the southern part of China between June and December, 2013. The samples included 41 starfruits, 38 wax apples and 38 Indian jujubes. The six cities, distributed within provinces of Hainan, Guangxi, Fujian and Guangdong, are the major tropical fruit growing regions of the country. Sampling localities covered plantations, wholesale markets, retail markets, supermarkets, and farmers' markets. The samples were maintained between 0 and 4 °C until arrival at the laboratory. Subsequently, the samples were chopped and homogenized in a commercial blender at high speed. Prepared samples were stored at −20 °C until analysis.

Samples were extracted and then purified according to the NY/T 761-2008 guidelines set by the Ministry of Agriculture (MOA) of China (MOA, 2008). Blended samples (25 ± 0.01 g) were weighed in a 150 mL glass beaker and mixed thoroughly with 50 mL of acetonitrile using a high speed homogenizer. The homogenate was allowed to settle, and the supernatant from each sample then passed through a filter paper into a 100 mL cylinder containing 6–7 g of NaCl. Each mixture was shaken vigorously by hand for 2 min and then allowed to settle for at least 30 min. From the supernatant, 10 mL were transferred into a 50 mL evaporation flask and evaporated to dryness using a vacuum rotary evaporator set at 36 °C. Each sample was reconstituted in 4 mL of dichlorolmethane/methanol (95/5 v/v). The NH_2 SPE cartridge was conditioned with 5 mL of dichlorlomethane/methanol (95/5 v/v) and loaded with the above sample extracts. The pesticides were eluted with 4 mL of dichlorolmethane/methanol (95/5 v/v) for three times. The SPE eluates were then combined and evaporated to dryness using a vacuum rotary evaporator set at 32 °C. Finally, the dry residue from each sample was re-dissolved in 5 mL of methanol/water (60/40 v/v), filtered through a 0.22 μm membrane and transferred into an autosampler vial for ultra-high performance liquid chromatography tandem mass spectrometry (UPLC-MS/MS) analysis.

2.3. Analysis by UPLC-MS/MS

For the identification and quantification of the nine analytes, the ACQUITY UPLC System (Waters, USA) coupled to the Quattro Premier XE (Waters, USA) triple quadrupole mass spectrometer with electrospray ionization was used. Chromatographic separation was performed on the ACQUITY UPLC BEH C18 column (50 mm × 2.1 mm; 1.7 μm) (Waters, USA) equipped with the ACQUITY UPLC BEH C18 guard column (5 mm × 2.1 mm; 1.7 μm) (Waters, USA) at 35 °C using gradient elution. Mobile phase A was an aqueous solution containing 1 mM of ammonium acetate, and mobile phase B was methanol. The gradient was initiated at 0 min with 10% eluent B for 0.01 min and continued with a linear increase to 70% eluent B within 1 min. This condition was maintained for 4.50 min, followed by another linear increase to 80% eluent B within 0.10 min. This condition was maintained for 1.00 min. A linear increase to 90% eluent B occurred within 4.00 min, and this condition was maintained for 2.50 min. Finally, the system returned to 10% eluent B within 1 min and was re-equilibrated for 1.50 min. The sample temperature was kept at 15 °C. The flow rate was 0.25 mL/min, and the injection volume was 5.0 μL.