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Short communication

Effect of Chinese traditional cooking on eight pesticides residue during cowpea processing

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ABSTRACT

Thermal processing can concentrate residues or convert residues to more toxic metabolites in food. Chinese traditional cooking pays more attention to thermal processing and more vegetables were eaten after thermal processing. In this study, the effect of Chinese traditional cooking (washing, blanching, stir-frying, frying and combined operations) on eight pesticides residues (pyridaben, procymidone, chlorothalonil, difenoconazole, α-cypermethrin, bifenthrin, S-fenvalerate and λ-cyhalothrin) in cowpea which was one of the most important legume crops in China was examined. Result showed washing and blanching could reduce residues with low K_{ow} while stir-frying and frying were more effective to residues with high K_{ow}; stir-frying and frying could concentrate residues with low K_{ow}; the residue levels in oil increased following increasing frying time and frequency especially the residues with high K_{ow}; one metabolite studied in this paper was not detected. Blanching (5 min) followed by stir-frying (3 min) was the most effective combined operation.

1. Introduction

Food safety induced by pesticide residues is a growing concern worldwide (Chen et al., 2014). Most agricultural products are not only consumed fresh, but also consumed after processing. Many studies have shown significant reductions in pesticide residues during household or industrial food processing (Ikeura, Hamasaki, & Tamaki, 2013; Mujawar, Utture, Fonseca, Matarrita, & Banerjee, 2014; Zhao, Ge, Liu, & Jiang, 2014). However, it should be noted that processing can concentrate residues or convert residues to more toxic metabolites in food like thermal processing (Zhao et al., 2014).

Cooking encompasses a vast range of methods depending on the customs and traditions, availability and the affordability of the resources (Kaushik, Satya, & Naik, 2009). For example, Chinese traditional cooking pays more attention to blanching, frying and "stir-frying". "Stir-frying" is the most popular cooking way in China and is also the main cooking way for Chinese food which is very popular in the world. Stir-frying is to quickly fry the raw food with a small amount of oil at high temperatures so as to maintain the natural colour and flavour of the raw food and keep the vegetables crisp and fresh while little moisture and nutrients are lost.

Cowpea (*Vigna unguiculata*) is one of the most important legume crops in China, with a total planting area of 330,000 ha (Li & Song, 2012). Based on the routine monitoring data in year 2011–2013 conducted by Ministry of Agriculture of China, eight pesticides (pyridaben, procymidone, chlorothalonil, difenoconazole, α-cypermethrin, bifenthrin, S-fenvalerate and λ-cyhalothrin) were detected at a high frequency on cowpea (Unpublished results). Compared to Europeans and Americans, Chinese people eat more vegetable, for example, vegetable comprises about 10% of the daily food intake (Zhu & Zhou, 2001). And compared to the "cold" cooking ways to vegetables in Europe and America where the vegetables are mainly eat freshly or as salad, more vegetables are eaten after thermal processing like stir-frying. So it was important, meaningful and necessary to study the effect of Chinese traditional cooking on the residues in vegetables of China. To the best of our knowledge, there are scare reports on this aspect.

In view of these facts, the effect of Chinese traditional cooking on eight pesticides residue during cowpea processing was examined. Actual exposure level of these pesticides and corresponding processing factors are calculated. Although the residue definitions of these eight pesticides for risk assessment and monitoring in food of plant origin are the parent compound or sum of isomers set by China (GB 2763-2014), one metabolite was detected before and after processing for tracking the residues and its toxicity. These data were useful for correctly assessing Chinese people's dietary

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exposure to these contaminants from cowpea. In addition, an effect cooking way to reduce residues intake is supplied according to the results.

2. Materials and methods

2.1. Chemicals and reagents

Certified pesticide standards and formulations were supplied by the Institute of Agro-Environmental Protection (Tianjin, China). PB-7(2-(4-{[(1-*tert*-butyl-5-chloro-6-oxo-1,6-dihydropyridazin-4-yl)sulphanyl]methyl}phenyl)-2-methylpropanoic acid), one metabolite of pyridaben, was purchased from Dr. Ehrenstorfer (Augsburg, Germany). The physicochemical properties of the pesticides are listed in Table 1. Acetone, *n*-hexane, acetonitrile, toluene, anhydrous magnesium sulphate ($MgSO_4$) and sodium chloride were AR grade and purchased from Guangzhou Chemical Reagent Factory (Guangzhou, China). For solid phase extraction, CNWBOND GCB/NH_2 (500 mg/500 mg, 6 mL) SPE cartridges and primary secondary amine (PSA, 40 μm Bondesil) were obtained from Anpel (Shanghai, China). Ultra-pure water was obtained from a Milli-Q system (Bedford, MA, USA).

2.2. Sample preparation and processing

Fresh cowpea pods without pesticides were collected from a farm of the Chinese Academy of Tropical Agricultural Sciences. An appropriate amount was used for the controls and the rest was submerged for 30 min in a solution containing the eight pesticide formulations followed by air-drying at room temperature in fume hood for 24 h. This procedure provided the initial deposits on the cowpea of 0.4–0.6 mg/kg, which were the levels detected during the routine monitoring.

The household processing procedure mimicked Chinese traditional cooking. Each process used 200 g cowpeas with three replicates.

2.2.1. Washing

The sample was placed in a plastic colander and rinsed under running tap water (1 L/min, 25 °C) for 0 (unprocessed), 1, 3 or 5 min, respectively.

2.2.2. Blanching

The sample was immersed in 1 L of boiling water (100 °C) in an uncovered pot. Three treatment times were set as 0 (unprocessed), 1, 3 and 5 min.

2.2.3. Stir-frying

The sample was cut into 3 cm pieces and added to an open wok in which 50 mL peanut oil had been preheated to 250–280 °C. Then 2–3 g table salt was added and the contents were stirred vigorously for 0 (unprocessed), 1, 2 and 3 min, respectively.

2.2.4. Frying

The sample was cut into 3-cm pieces and added into an open wok in which 500 mL peanut oil had been preheated to 210–240 °C. The contents were then stirred gently for 0 (unprocessed), 30, 40 or 50 s, respectively.

After the exposure of "gutter oil" event in China, Chinese families pay more attention to the safety of cooking oil. Except some fast food restaurants, common Chinese families generally refused to use cooked oil even the oil used for frying once. But considering in some places the oil could be reused, the oil after frying for each replicate of each treatment was collected respectively and the pesticide residues and the metabolite in the fried oil were detected. After cooling to room temperature, the residual oil was weight and stored at −20 °C for residue analysis. In order to see the residue levels varied upon repeated frying, the residue levels of the eight pesticides in the oil after frying one, two and three batches of cowpea were determined, respectively (three times was generally the biggest frequency for the reused oil for frying in China). Each batch of cowpea was 200 g and the frying time for each batch was 50 s.

2.2.5. Combined operations

Vegetables are typically washed or blanched before stir-frying or frying in China. Based on the results of each individual operation above, the individual operations which had most effective removal with shortest time to the residues were combined according to the actual practice in China: washing (3 min) + stir-frying (3 min); blanching (5 min) + stir-frying (3 min); washing (3 min) + frying (50 s).

In order to avoid cross pollution, each replicate used fresh oil or boiling water; the woks and knives were cleaned with detergent, tap water, acetone and ultra-pure water in turn before use. After cooling to room temperature, the cowpea samples were wiped with filter paper to remove excess liquids (water or peanut oil), then weight, cut into pieces (0.5 cm or less) and stored in polypropylene bottles at −20 °C.

2.3. Extraction, purification and determination

Eight parent compounds and one metabolite in cowpea before and after processing with different treatment were extracted and purified according to Agricultural Standards of China (NY/T 761-2008). Due to the more lipophilic oil matrix, a modified QuEChERS method was used for extraction and purification these compounds from oil before and after frying with different treatment as described by Anastassiades, Lehotay, Stajnbaher, and Schenck (2003).

Table 1
Physicochemical properties of pesticides.

Pesticide	Systemic	Water solubility[a] (mg L^{-1})	Melting point (°C)	Boiling point[b] (°C)	Decomp temp[c] (°C)	Log K_{ow}	Vapour pressure[d] (Pa)
Pyridaben	No	0.012*	111–112	429.9	200	6.37	2.5×10^{-4}*
Procymidone	Yes	3.3	163–164.5	477.9	360	3.3	2.3×10^{-5}
Chlorothalonil	No	0.81	252	350	>350	2.9	7.6×10^{-5}
Difenoconazole	Yes	15	82–83	547	>572	4.4	3.3×10^{-8}
α-Cypermethrin	No	0.01*	80–82	826	270	6.3	2.1×10^{-5}*
Bifenthrin	No	0.0001	65–70	744.4	285	6.0	2.4×10^{-5}
S-Fenvalerate	No	0.001*	59–60	539	249	6.2	1.2×10^{-6}*
λ-Cyhalothrin	No	0.004*	47–49	498.9	275	6.9	2×10^{-7}*

[a] The values marked with "*" are the water solubility at 20°C while the other values without "*" are the water solubility at 25°C.
[b] At 760 mmHg.
[c] Decomposition temperature.
[d] The values marked with "*" are the vapour pressure at 20°C while the other values without "*" are the vapour pressure at 25°C.