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Risk assessment of pesticide residues in dietary intake of celery in China

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ABSTRACT

Objective: Residue risk assessment of pesticides in celery was conducted to provide a scientific basis for agricultural regulation policies and working procedures.
Methods: Three hundred samples from eight main growing regions in China were collected and pesticide residue analyses were performed using GC–MS/MS and LC-MS/MS methods. Both chronic and acute intake risk of pesticides were assessed. Furthermore, intake risk of each detected pesticide was ranked according to a predefined ranking matrix.
Results: (1) Out of these 300 samples, 175 were revealed to contain one or more pesticide residues. Twenty-five pesticides were identified in total, out of which, carbofuran was found to exceed the maximum residue limit. (2) Chronic and acute intake risks were evaluated and lie in between 0 and 1.80 and between 0.05 and 28.0 for these twenty-five pesticides, respectively. (3) Intake risk of individual pesticide was ranked; five pesticides, including avermectin, triazophos, chlorpyrifos, dimethoate oxygen, and carbofuran posed the highest risks.
Conclusion: Pesticide residues were detected in more than 58% celery samples in our study. Most pesticides have a residue level lower than their maximum residue limit and pose low chronic and acute dietary intake risk. However, usage of some pesticides like carbofuran should be closely monitored and regulated in the future.

1. Introduction

Food safety has become a major concern in China. Pesticide and antimicrobial residue is a main contributing factor and poses a dietary intake risk to human health. Celery is a popular and low-calorie vegetable consumed all over the world. It has potential benefit for the digestive tract and cardiovascular system and possible for weight loss or management (Clegg and Cooper, 2012). By 2009, celery growing reached 8.4×10^6 acres in China, which is accounting for 3.1% of overall vegetable acreage, and celery production is 2.1×10^7 tons, which is appropriately 3.4% of all vegetable consumption (Crop Production Bureau of China Ministry of Agriculture, 2014). In the U.S., the major regions of celery crop, California and Michigan, harvested more than 28,000 acres of celery and 18 million cwt was produced in 2014 according to the USDA (National Agricultural Statistics Service and United States Department of Agriculture, 2014).

Like other agricultural produces, pest, weed and disease control are critical for celery industry; chemicals, including pesticides, herbicides and antimicrobials, are commonly used for celery crops. For example, aster leafhopper is a common carrier of viruses and spreads diseases like aster yellows disease (Jensen, 1959). The plants infected with this disease cannot be cured and have to be removed. Chlorantraniliprole is one of the pesticides used to control aster leafhoppers (Mazzi and Dorn, 2012). Although it is beneficial to celery crops, it is toxic to bees and birds and has the potential for contaminating ground water (Sial and Brunner, 2012). More importantly, its residues on the dietary celery may harm the consumer's health (Sial and Brunner, 2012).

We chose celery as our model system because celery is

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subjected to high pesticide residues relative to other vegetables (Wu et al., 2010). Studies on pesticide residues in celery represent one of the "worst" cases on pesticide control in general. Namely, if consumption of celery is safe, consumption of other "clean" vegetables should pose a better prospective. Risk assessment of pesticide residues is necessary and such reports were recorded in many countries and regions (Australian Pesticides and Veterinary Medicines Authority, 2004; Chun and Kang, 2003; Drouillet-Pinard et al., 2011; Environmental Working Group, 2014; European Food Safety Authority, 2013; M. A. Z. Chowdhury, 2014; Sarikurkcu et al., 2011; Seo et al., 2013; Tucker, 2008; USDA et al., 2014; Wu et al., 2010). In one of the reports from USDA and FDA, it is found that as many as 57 pesticides are detected in celery, which is regarded as one of the "dirtiest" vegetables (Environmental Working Group, 2014; USDA et al., 2014).

In China, researchers and governmental agencies have realized the necessity of such studies, not only on identifying pesticide residues, but also on evaluating the acute and chronic risk to consumer (Bai et al., 2006; Chen et al., 2011; Shen et al., 2005; Wu et al., 2010; Zhang et al., 2011). Wu et al. (Wu et al., 2010) evaluated the pesticide residues in celery in 2010 and found that pesticide residues in celery are significantly higher than other vegetables. In their study, they only used celery samples from Shanxi province. There are no systematic and national wide studies that have been carried out on risk assessment of pesticide residues in celery.

This study is aimed at evaluating the dietary risk of pesticide residues in celery consumption in China, in order to establish practical guidelines and monitor the usage of pesticides in celery industry. Both chronic (M. A. Z. Chowdhury, 2014; Seo et al., 2013) and acute (Sarikurkcu et al., 2011; Tucker, 2008, p. -) intake risk were assessed. Furthermore, we ranked the exposure risk of pesticides in celery consumption using a matrix ranking method developed by the Veterinary Residues Committee of UK (The Veterinary Residues Committee – Matrix Ranking Subgroup, 2013).

2. Materials and methods

2.1. Chemical and reagents

Acetonitrile and sodium methoxide (HPLC grade) were purchased from Fisher Scientific (Waltham, MA, USA). Toluene and dichloromethane (Analytical grade) were purchased from Sinopharm Chemical Regent Co., Ltd (Shanghai, China). All solvents were passed through a 0.22 μm cellulose filter from Membrane Solutions (Dallas, TX, USA).

2.2. Sample collection

Three hundred celery samples were collected from eight main growing regions of celery crops in China, including Shandong, Hebei, Jiangsu, Henan, Anhui, Hubei and Shannxi and Sichuang provinces. Celery farms in these eight regions account for 66.2% of total celery acreage in China (Crop Production Bureau of China Ministry of Agriculture (2015)). All samples were sealed in proper containers and stored at −20 °C until analysis.

2.3. Sample preparation

2.3.1. Extraction

Samples were prepared according to a procedure described elsewhere (AQSIQ and SAC, 2009, p. 4, 2007, p. 500). 25 g of each celery sample composed of all edible parts was homogenized with 100 ml acetonitrile using T25 Basic high-speed homogenizer (Ika Work Inc, Staufen, German) for 1 min. The extract was transferred into a stoppered cylinder filled with 10 g NaCl and was vertexed for 1 min. After centrifugation for 30 min, 20 ml of the supernatant was transferred into a pear-shaped evaporating flask and dried by a rotary evaporator (Heidolph LABOROTA 4001, German).

2.3.2. Pre-cleaning for GC–MS analysis

The sample was pre-cleaned by an amino column (Cleanert NH2-SPE, Agela technologies, Tianjin, China) pre-equilibrated by 5 ml eluent (acetonitrile:toluene = 3:1, v/v). The pre-cleaning procedure is described as following. First, the dried sample was re-dissolved by 2 ml eluent and loaded onto the column. To completely transfer the sample to the column, this step was repeated three times. The flask was then rinsed by 20 ml eluent which was gradually transferred to the column. The collected eluate was placed on a nitrogen dryer to remove the excessive solvent. The sample was re-dissolved in 2 ml hexane.

2.3.3. Pre-cleaning for LC-MS/MS analysis

Extraction of celery samples was performed as the same as in 2.3.1. The same pre-equilibrated column was used for pre-cleaning procedure, but with a different eluent (dichloromethane: methanol = 99:1, v/v). The sample was concentrated and transferred to the column as the same as in 2.3.2. The sample was dried under nitrogen gas and re-dissolved in 1 ml of methanol. The sample was mixed with 1 ml pure water by vertexing for 30 s and then was filtered by passing through a 0.22 μm cellulose filter from Membrane Solutions (Dallas, TX, USA).

2.4. GC–MS/MS

GC–MS/MS analyses were conducted on a TSQ Quantum XLS (Thermo Fisher Scientific, San Jose, CA, USA) using a DB-5MS column (30 m × 0.25 mm × 0.25 μm, Agilent Technologies, Santa Clara, CA). The oven temperature was programmed at 60 °C for 2 min, increased gradually to 150 °C at a rate of 15 °C/min and to 280 °C at 6 °C/min, and held for 8 min. The inlet temperature was at 250 °C. Injection volume was at 1 μl in splitless mode. The carrier gas was helium at flow rate of 1.0 ml/min. The mass spectrometer was operated in MRM mode with nitrogen as collision gas at flow rate of 1.5 ml/min. The temperatures of ion source and transfer line were at 230 °C and 280 °C. The solvent delay was set at 6.0 min.

2.5. LC-MS/MS

LC-MS/MS assays were performed on a 6460 Triple Quadrupole LC/MS (Agilent Technologies) with ZORBAX Eclipse Plus C18 column (50 mm × 2.1 mm, 1.8 μm, Agilent technologies, Santa Clara, CA). The mass spectrometer was equipped with ESI source and operated in positive/negative mode. Mobile phase was composed of water (solvent A) and methanol (solvent B) at a flow rate of 0.3 ml/min. The drying gas flow was at 8 l/min and the oven temperature is at 30 °C. Solvent B was initially set at 25% for 1.5 min; solvent B was brought to 55% from 1.5 to 3 min and kept at 55% for 2 min. Then, solvent B was increased to 90% from 5 to 8 min, brought back to 25% from 8 to 10 min, and kept at 25% for 2 min.

Pesticide residues were analyzed by either LC-MS/MS or GC–MS/MS method. When the residual amount of a pesticide in a sample is lower than the lower limit of quantification (LLOQ), the detected value was set at ½ of the LLOQ value (World Health Organization, 2010).

The calibration curve was acquired using standard solutions for preparation of celery samples. 0.01 μg/ml standard solution of pesticides (n = 3) was used to measure recoveries. The Limit of Detection (LOD) and Limit of Quantification (LOQ) were determined using the standard solution of analytes, and calculated as the value of three and ten times of the signal-to-noise ratio, respectively.

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