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Concentrations of organophosphorus pesticides in fresh vegetables and related human health risk assessment in Changchun, Northeast China

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A B S T R A C T

This study was designed to investigate organophosphorus pesticides (OPs) concentrations in fresh vegetables and estimate potential health risks to inhabitants. A total of 214 samples of seven types of vegetables were collected from Changchun, the capital of Jilin province, one of the most important vegetable production areas. The eleven OPs were analyzed by gas chromatography coupled with flame photometric detector (GC-FPD). Results showed that 23.4% of samples contained OPs above maximum residue limit (MRL), 68.7% of samples below MRL and only 7.9% of samples were found free of OPs. Detection rates of OPs decreased in the following order: diazinon (82.2%) > phorate (45.8%) > dimethoate (29.4%) > parathion-methyl (27.6%) > omethoate (23.8%) > dichlorvos (22.9%) > fenitrothion (21%) > fenthion (18.7%) > parathion (18.2%) > methamidophos (17.3%) > malathion (12.1%). The OPs levels were higher for leafy than for non-leafy vegetables. The percentages of OPs above MRL: welsh onion (82.5%) > radish (37.5%) > pepper (17.2%) > Chinese cabbage (14.3%) > cucumber (3.2%) > eggplant (2.9%) > tomato (0%). 49.5% samples contained two or more OPs. The average target hazard quotients (ave THQ) were all less than one and the average Hazard Index (ave HI) for adults and children were 0.448 and 0.343, respectively. It is concluded that inhabitants who are exposed to average OPs levels may not be endangered by health risk.

1. Introduction

Organophosphorus pesticides (OPs) were widely used to control various insects on crops due to high toxic and moderate persistence. In 2010, insecticide demand of China reached 129,500 tons, among which 72% were OPs (Li, Mehler, Lydy, & You, 2011). Studies have linked OPs exposure with headaches, allergies and nausea, adverse physiologic effects, increased frequency of cancer, neurobehavioral and cognitive abnormalities, teratogenicity, endocrine modulation and immunotoxicity (Alavanja, Hoppin, & Kamel, 2004; Bouchard et al., 2011; Engel et al., 2011; Handal, Lozoff, Breilh, & Harlow, 2007; Jurewicz & Hanke, 2008).

Vegetables constituted a major part of human diet, which contribute to human's required nutrients, fiber and vitamins (Swarnam & Velmurugan, 2013) yet are the main exposure pathway of OPs to human body (Sapbamrer & Hongsibsong, 2014; Teresa Munoz-Quezada et al., 2012). Chen et al. (2012) reported that application of pesticides at the recommended dose on vegetables is unlikely to pose any public health issues as long as it is applied according to good state agricultural practices. In order to increase yields of vegetables, OPs weren't applied properly according to their recommended dosages and usage frequency during growing seasons of vegetables (Zhang, Liu, Yu, Zhang, & Hong, 2007). Previous reports on OPs levels of vegetables in China are available (Bai, Zhou, & Wang, 2006; Li, Tai, Liu, Gai, & Ding, 2014; Wang, Liang, & Jiang, 2008). Toxic OPs, such as methamidophos, parathion-methyl, and parathion, had been banned since 2007 for agricultural use in China owing to their acute toxicity to human. However, in China, to ensure safety of fresh agricultural product is still a great challenge, as prohibited pesticides were detected in vegetables (Shang, Sun, & Zhang, 2011; Szpyrka et al., 2015; Wang, Wang, Huo, & Zhu, 2015; Zhou & Jin, 2009), which are likely to cause potential human health and environmental impacts.

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Therefore, there is an increasing human health concern of OPs from vegetables because many vegetables can be eaten raw (Sapbamrer & Hongsibsong, 2014; Sun, Horng, Hsieh, Wang, & Lee, 1977; Torres, Pico, & Manes, 1996).

The collected vegetable samples (Chinese cabbage, radish, tomato, eggplant, pepper, cucumber and welsh onion) grow in the vicinity of Changchun, which covered an area of about 4,906 km^2, with an urban population of more than 3.6 million. The vegetable planting area and yield in this region were about 120 km^2 and 0.35 million tons, respectively (Jilin Statistics Bureau, 2012). OPs concentrations in vegetables varied with seasons. Bhanti and Taneia (2007) reported that winter vegetables in northern India are the most contaminated followed by summer and rainy vegetables due to low temperature and short day length. We only collected vegetables in autumn due to budget constraints. However, autumn vegetables collected from Northeast China have stronger representativeness because these vegetables were mainly produced for home consumption and sold to residential areas of urban and suburban regions. On the other hand, autumn vegetables were mainly used to reserve for and eat throughout the entire winter, and even spring. However, information about OPs in autumn vegetables of Changchun was scarce.

The purposes of this study were 1) to quantify the concentrations of OPs in fresh vegetables, 2) to calculate the estimate dietary intake (EDI), target hazard quotient (THQ) and hazard index (HI) of OPs for adults and children to evaluate the health risk through vegetables consumption. The importance of this work is still reflected by the fact that data on OPs residues in vegetables are quite scarce and difficult to obtain in many regions of the world.

2. Materials and methods

2.1. Study area

Changchun is located in Jilin province, Northeast China (43°43′ N, 125°19′ E), which is the most important and largest producer of agricultural crops and a key commodity grain base (Fig. 1). The climate of Changchun is a typical continental monsoon, which characterized by long and cold winters and generally shorter and warmer summers. The average annual temperature is 4.8 °C with the highest temperature 39.5 °C in summer, the lowest temperature −39.8 °C in winter. Average annual rainfall is 569.6 mm, and more than 70% of the rainfall occurs in June, July and August. The frost-free period lasts about 130–140 days. The mean annual evaporation is about 1000 mm. The soils are black soil (Luvic Phaeozem, FAO), chernozem (Haplic Chernozem, FAO) and meadow soil (Eutric Vertisol, FAO).

2.2. Vegetables sampling

Suburban of Changchun was divided into cells of 1 × 1 km in size and then screened out 54 typical open vegetable fields (Fig. 1). All the sample sites were recorded using a hand-held Global Positioning System (GPS). From 25 August to 5 September 2014, a total of 214 samples of seven types were collected, (Chinese cabbage *Brassica campestris* L. ssp. *pekinensis*(Lour.)Olsson, welsh onion *Allium fistulosum* L. var. *giganteum* Makino, cucumber *Cucumis staivus* L., pepper *Capsicum annuum* L., eggplant *Solanum melongena* L., tomato *L*ycopersicon esculentum Mill, and radish *Raphanus sativus* L.) of commonly consumed vegetables. Only edible parts of each sample were collected in triplicate from the surroundings of each site and mixed thoroughly to obtain a bulk sample. About 1.0 kg of bulk sample was immediately wrapped in aluminum foil, transported to the laboratory and stored for 24 h at 4 °C until the analysis.

2.3. Vegetables analysis

The extraction and cleanup method was conducted according to the Chinese standard method (NY/T 761-2008). The edible parts of fresh vegetable samples were prepared with a knife and mixed thoroughly with food chopper. Briefly, 25.0 g of homogenized vegetable sample and 50.0 ml acetonitrile were weighed respectively and mixed in the conical flask. The mixture was blended by a mixer for 2 min at 15,000 rpm, and was then filtered to the mixing cylinder with stopper. The 10.0 g sodium chloride was poured into the cylinder. After shaking, the mixing cylinder was left to have distinct layers for 30 min. The 10.0 ml of upper layer was taken into round bottom flask, concentrated to dryness by rotary evaporator at 40 °C and the residues were dissolved in 2 ml of acetone. Analysis of information obtained without cleanup procedure was reported by Gobo, Kurz, Pizzutti, Adaime, and Zanella (2004), Torres et al. (1996) and Quintero et al. (2008). The application of this method helps reduce costs and time of analysis.

The OPs were analyzed by a gas chromatography (Shimadzu GC-2010plus, Japan) with Flame Photometric Detector (FPD), equipped with RTX-5 (30 m, 0.25 mm i.d. and 0.25 μm film thickness, USA). Injection and FPD temperatures were set to 250 °C and 280 °C, respectively. 1 μl (splitless) of sample was injected into the GC in the phosphorus mode. Nitrogen gas was used as the carrier with a velocity of 30.0 cm s^{-1}, while hydrogen (85.0 ml min^{-1}) and air (110.0 ml min^{-1}) were used for the FPD. The temperatures programmed of GC were set as follows: initial temperature at 120 °C for 3.0 min, ramping to 270 °C at 5 °C min^{-1}, and holding for 10 min. The entire duration was 43.0 min. Retention time was used to identify correct peak on the chromatogram. The quantity of each OP was calculated by applying the external standard method and these values were based on fresh basis. OPs analyzed in vegetable samples included diazinon, phorate, dimethoate, parathion-methyl, omethoate, dichlorvos, fenitrothion, fenthion, parathion, methamidophos and malathion. It should also be noted that no monitoring study can detect all pesticides. However, most of the pesticides identified as those that are commonly in use were included.

Mixed standards of OPs were presented by Institute of Environmental Protection and Monitoring, Minister of Agriculture, China. The results of quality assurance were listed in Table 1. The recoveries were 91.4–105.2% for eleven OPs and the limit of detection (LOD) that calculated by using a signal-to-noise (S/N) ratio of three was in the range 5–20 ng ml^{-1}. All solvents were of pesticide grade. Each analysis for quality assurance purpose was performed in triplicate.

2.4. Human risk assessment of OPs through vegetables consumption

2.4.1. Estimated daily intake (EDI)

The EDI dependent on both individual OP concentration and the daily consumption of food (Zhuang, McBride, Xia, Li, & Lia, 2009). The EDI (μg kg^{-1} d^{-1}) was calculated as follows:

$$EDI = C \times C_{on}/Bw$$

Where C (μg kg^{-1}) was the average OPs concentration in all collected vegetables, C_{on} (kg $person^{-1}$ d^{-1}) was the daily average consumption of vegetables in the region, Bw (kg $person^{-1}$) represents body weight. Based on the report by Zheng et al. (2007), the average vegetables consumptions for adults and children were 242.0 and 108.5 g d^{-1} respectively, and the average body weights for adults and children were 55.9 and 32.7 kg, respectively.

2.4.2. Target hazard quotient (THQ)

According to standard USEPA methods, the risk of non-