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Human health risk assessment of DDTs and HCHs through dietary exposure in Nanjing, China

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HIGHLIGHTS

- Comprehensive food samples were collected in Nanjing, China.
- Monte Carlo simulation was used to assess dietary intake and health risk.
- Both non-cancer risk and cancer risk for different groups in Nanjing were assessed.
- Distributions of both exposure and risk were depicted for different groups in Nanjing.

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ABSTRACT

In a market based study in Nanjing, a typical southeast city in China, the most common consumed 23 kinds of foods from eleven different categories (vegetable, fruit, fish, pork, livestock meat, chicken, egg, milk, oil, rice and flour) were sampled in November 2015. The concentrations of DDTs and HCHs in foods were analyzed using gas chromatography with mass spectrometer detector. The residual amounts of DDTs and HCHs in foods were 0.95–3.53 ng g^{-1} and 0.32–1.96 ng g^{-1}, respectively. The highest residual of $\sum_{10}$OCPs was 4.75 ng g^{-1} in livestock meat and the lowest was 1.31 ng g^{-1} in flour. Estimated daily intakes of both DDTs and HCHs for children were higher than other age groups regardless of the gender. With respect to food categories, the consumption of vegetables generated higher dietary exposure of DDTs and HCHs than other food categories for all age categories, which accounted for 20.21%–29.18% of the total. The daily intakes of γ-HCH and DDTs for all population groups were far below the acceptable amounts suggested by the Food and Agriculture Organization of the United Nations/World Health Organization. Health risk assessment indicated that there was no obvious non-cancer risk for local residents, whereas the cancer risk was estimated to be from 10^{-6}~10^{-4}, being higher than the acceptable risk level and lower than the priority risk level. Among residents of different gender and age, females showed higher risk than males in all age groups, and children were the most vulnerable age group to health risk.

1. Introduction

Organochlorine pesticides (OCPs) are man-made highly persistent lipophilic organic pollutants introduced in the environment in the late 1940s. Typical compounds of OCPs are dichlorodiphenyltrichloroethane and metabolites (DDTs) and hexachlorocyclohexane isomers (HCHs), which have longer half-life and can transfer through the food chain to induce harmful effects for humans (Minh et al., 1999). Concerns about the carcinogenic and endocrine-disrupting characteristics of OCPs have led to a global ban on the use of OCPs. DDTs and HCHs have been banned in many developing countries since 1970s, and have been banned for more than 30 years in China (Zhao et al., 2003). Even so, there are still many illegitimate producers and subsequent use in many areas (Teng et al., 2012; Dallaire et al., 2013; Köhler and Triebskorn.,

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In general, dietary intake is the main source of environmental exposure of DDTs and HCHs (Van den Berg, 1994; Guo et al., 2005). It has been estimated that over 90% body load of DDTs and HCHs in the general population was derived from foods, particularly fatty food of animal origin (Chung et al., 2008). Therefore, there is an increasing concern about the residual concentrations of DDTs and HCHs in foods. DDTs and HCHs have been detected in many categories of foods, including vegetable, fruit, milk, oil, egg, etc (Wang et al., 2012; Akoto et al., 2015; Robinsona et al., 2016). The food of animal origins contained higher concentrations of DDTs and HCHs than other categories of foods (Wang et al., 2011). In recent research, the residual concentration of DDTs and HCHs in vegetables in Delhi has exceeded the level of maximum residue limits (MRLs) (Chourasiya et al., 2015). Thus, it is essential to pay attention to the pollution level and the corresponding health effects of DDTs and HCHs in foods. Reports concerning health risk assessment of DDTs and HCHs in comprehensive food categories based on the market basket data are limited (Wang et al., 2011; Stewart et al., 2011). Most previous studies sampled only one or some categories of foods (Shi et al., 2013; Cheng et al., 2014; Li et al., 2014; Akoto et al., 2015), and could not reflect the actual health hazards of DDTs and HCHs due to incomplete food categories.

Nanjing, the capital of Jiangsu Province, is a typical southeast city in China with more than 8 million residents. A previous study indicated that the detection rate of DDTs and HCHs in vegetables in Nanjing was 100% in 2005 (Gao and Jiang, 2005). There are no current reports on dietary exposure and risk assessment of DDTs and HCHs in Nanjing, leaving an information gap.

The objectives of this study were to investigate (1) the residue level of DDTs and HCHs in foods in Nanjing, (2) the daily dietary exposure level of DDTs and HCHs for different population groups in Nanjing, (3) the induced non-cancer and cancer risk for local residents.

2. Material and methods

2.1. Sampling

In November 2015, 23 kinds of foods from eleven different categories were purchased in representative supermarkets and wholesale markets in Nanjing, China. These included vegetable (green vegetable, Chinese cabbage, radish, cauliflower, carrot, cabbage, potato), fruit (banana, apple, pear, orange), fish (snakehead, weever, chub), chicken, pork, livestock meat (beef and mutton), egg, milk, oil, rice and flour, which have previously been determined to be the primary foods consumed by local residents. We collected twenty-five samples for each kind of food and created five composites for analysis. Only edible parts of each foodstuff were surveyed in this study. All collected samples were transported to laboratory as soon as possible and preserved at −15 °C before experimental analysis.

2.2. Analytical procedure

Each sample of 10 g wet weight was mixed with 20 ml acetonitrile solvent, and then was subjected to microwave extraction system (MES) (MARS2Xpress, CEM, USA). The vessels were heated in the microwave oven to 100 °C at 10 °C/min and held for 10 min. After extraction, the contents in the vessels were transferred to the centrifuge and were centrifuged 3 times at 1800 r/min prior to press filtering. Then 100 ml 4% sodium sulfate solution was added into a separating funnel with the eluent and the mixture was extracted twice with 30 ml *n*-hexane. After extraction, total extracts were concentrated to 1 ml using a vacuum rotary evaporator (R-201, Shanghai, China) with a 37 °C water bath, and were transferred to the alumina silica gel column which was eluted with 20 ml of *n*-hexane followed by 70 ml of dichloromethane at a rate of 2 ml/min. The eluate dichloromethane from the column during cleanup was first concentrated to near dryness in the vacuum rotary evaporator using a 37 °C water bath. The residue was then transferred and diluted with *n*-hexane and brought to exactly 1 ml by nitrogen blowdown (Eyela MG-1000) at room temperature (25 °C). The samples were sealed in vials and stored at −4 °C before analysis.

The concentrations of DDTs and HCHs were determined by using gas chromatography-mass spectrometry (QP2010, Shimadzu, Japan) with a 30 m × 0.25 mm i.d. × 0.25 μm film thickness HP-5MS capillary column. GC temperature was programmed from an initial 60 °C before commencing at 5 °C/min up to 280 °C, with a final holding time of 20 min. Helium was used as the carrier gas and operated in splitless mode at a flow rate of 1 mL/min. The head column pressure was 30 kPa. The mass spectrometer was operated in SIM mode with an electron impact ionization of 70 eV, an electron multiplier voltage of 1288 V, and an ion source of 230 °C. Concentrations were determined for 10 compounds in all samples. They were α-HCH, β-HCH, γ-HCH, δ-HCH, o,p'-DDE, p,p'-DDE, o,p'-DDD, p,p'-DDD, o,p'-DDT, p,p'-DDT.

2.3. Quality control

All solvents used were chromatography purity. Alumina and silica gel (80–200 mesh; Dikma, China) were heated at 650 °C in a muffle furnace (DLII-9, Beijing, China) for 10 h, kept in a sealed desiccator, and reactivated at 130 °C for 4 h immediately prior to use. All glassware was cleaned using an ultrasonic cleaner (KQ-500B, Kunshan, China) and heated to 400 °C for 6 h. The concentrations of DDTs and HCHs were calculated by a five-point calibration curve with linearity higher than 0.99 for all target compounds. The laboratory procedure blanks were determined by going through the extraction and cleanup procedures using glass beads. The measured procedure blanks were mostly more than 1 order of magnitude lower than the sample measurements. All the results of food samples were laboratory procedure blank corrected. Recovery of individual HCHs ranged from 78.9% to 106.3%, and DDTs ranged from 87.1% to 111.2%. Data analyzed in the article were not corrected for recoveries. The detection limit for HCHs and DDTs in different food samples is 0.01–0.33, 0.01–0.26 ng g^{-1} wet weight, respectively.

2.4. Dietary exposure and cancer risk assessments

The population of Nanjing was divided into eight groups according to age and gender: children (4–10 y), adolescents (11–17 y), adults (18–60 y), and seniors (61–70 y) of male as well as the above groups of female.

As typical organochlorine pesticides, DDTs and HCHs have been extensively used in China. Many studies indicated that DDTs and HCHs have been propagated in organisms by food chains and accumulated high level (Xu et al., 2003). Therefore it's necessary to determine the dietary exposures of DDTs and HCHs (Annette et al., 2009). The estimated daily intake (EDI) of DDTs and HCHs in foods was calculated according to the following equation:

$$EDI = (C \times CR)/B_W \quad (1)$$

Where EDI is the estimated daily intake ($ng \cdot (kg \cdot d)^{-1}$), C is the concentration of pesticide ($ng \cdot g^{-1}$.wet) (SI, Table S1), CR is the consumption rate ($g \cdot d^{-1}$) (SI, Table S4) and B_W is the body weight (kg) (SI, Table S5). We treated C, CR and B_W, which followed log-normal, normal and normal distribution, respectively, in Eq. (1)