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Parent and halogenated polycyclic aromatic hydrocarbons in farmed cockroaches and implications for human exposure

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ABSTRACT

Medicinal insects have been widely used to cure human diseases for ages. Nevertheless, knowledge about the toxic chemicals accumulated in medicinal insects and their effects on human health was insufficient. In the present study, sixteen priority polycyclic aromatic hydrocarbons (PAHs) and nine halogenated PAHs (HPAHs) were determined in farmed medicinal cockroaches to address this issue. Total concentrations of PAHs in young nymphs, old nymphs, and adults ranged from 162 to 1025, 252 to 967, and 267 to 1168 ng/g, respectively. Levels of the sum of HPAHs varied from 0.84 to 9.17, 1.86 to 5.21, and 1.01 to 8.60 ng/g for young nymphs, old nymphs, and adults, respectively. The daily intake and excess cancer risk of PAHs and HPAHs were calculated for people who take cockroach-related drugs. Our results indicated that females and children have slightly higher exposure levels from the perspectives of gender and age, respectively. The estimated excess cancer risk of PAHs and HPAHs were both lower than the priority risk level (10^{-4}), indicating a low potential carcinogenic risk with the medicinal cockroach consumption.

1. Introduction

As the biggest group of animals on the earth, insects are considered to be one of the important biological resources that have not been fully developed and utilized by human beings (Zhang et al., 2008). Medicinal use of insects is one of the important and successful ways to utilize insect resources (Ding et al., 1997). Not only insects themselves have played mystical and magical roles in the treatment of several illnesses, but the substances extracted from their bodies have been used as medicinal resources by human cultures all over the world (Costa-Neto, 2005). Cockroaches are an important kind of medicinal insects. Among the 3500 known species of cockroaches, many of them have significant medicinal value for human beings (Zhang et al., 2008). Unlike its endangered species counterparts, such as seahorse, turtle shell, rhinoceros horn, and tiger penis, cockroaches are easier to find and farm. For example, the wingless cockroaches, such as *Eriocheir sinensis* and *Orosius orientalis*, are two main species farmed in China and commonly used in traditional Chinese medicines as components of some traumatic or vulnerary medicines (Zhang et al., 2008). Until now, cockroaches have been used to cure as much as 30 medical conditions of human beings, such as boils, indigestion, warts, and heart disease (Zschunke, 1978; Baumholtz et al., 1997).

However, toxic chemicals accumulated in these medicinal insects may lead to human health risks when they were used to produce medicines. Polycyclic aromatic hydrocarbons (PAHs) and halogenated PAHs (HPAHs) are a group of ubiquitous toxic organic contaminants (Ma et al., 2013a,b; Qin et al., 2013; Sun et al., 2013; Zheng et al., 2014). Due to their toxic, mutagenic, and carcinogenic potentials, PAHs and HPAHs are an important matter of concern for public health (Ma et al., 2009; Ding et al., 2012, 2013; Ni and Zeng, 2012; Pieterse et al., 2013). So far, knowledge about the human exposure levels and health risks of toxic chemicals accumulated in medicinal insects was limited. In the present study, sixteen PAHs and nine HPAHs in cockroaches farmed in China were determined to give some implications for human exposure to toxic chemicals accumulated by this medicinal insect. The main objectives of the present study were to (1) measure the levels of PAHs and HPAHs in farmed medicinal cockroaches; (2) estimate the daily intake of PAHs and HPAHs; (3) evaluate the potential health risk induced by PAHs and HPAHs via cockroach consumption.

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2. Materials and methods

2.1. Chemicals

A standard solution of the 16 U.S. Environmental Protection Agency priority PAHs of the highest purity available was purchased from Chem Service, Inc. (West Chester, PA), including naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fle), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), chrysene (Chr), benzo[a]anthracene (BaA), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-c,d]pyrene (InP), dibenzo[a,h]anthracene (DBA), and benzo[g,h,i] perylene (BghiP). Internal standards (2-fluorobiphenyl and p-terpheny-d_{14}) and surrogate standards (naphthalalene-d_8, acenaphthylene-d_{10}, phenathrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}) were purchased from Dr Ehrenstorfer Gmbh (Augsbury, Germany). 9-chlorophenanthrene (9-ClPhe), 2-chloroanthracene (2-ClAnt), and 9,10-dichloroanthracene (9,10-Cl_2Ant) were purchased from Aldrich (St. Louis, MO). 1-bromopyrene (1-BrPyr), 2-bromofluorene (2-BrFle), 9-bromophenanthrene (9-BrPhe), 9-bromoanthracene (9-BrAnt), and 9,10-dibromoanthracene (9,10-Br_2Ant) were obtained from Acros Organics (Geel, Belgium). 7-bromobenz(a) anthracene (7-BrBaA) was purchased from Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan). Neutral silica gel (80–100 mesh) and alumina (80–100 mesh) were Soxhlet-extracted with methanol for 24 h and then with dichloromethane for another 24 h. Extracted silica gel and alumina were activated for 12 h at 180 °C and 250 °C, respectively, and then deactivated with distilled water (3%, w:w) prior to use. All organic solvents used were redistilled using a glass system. In addition, all glasswares were hand-washed with detergent and tap water, rinsed with deionized water, and baked at 450 °C for at least 4 h prior to use.

2.2. Samples collection and preparation

According to different life cycles, 60 farmed cockroach samples, *Periplaneta americana*, including 20 young nymphs, 20 old nymphs, and 20 adults were purchased from a feedlot located in Xuzhou, Jiangsu Province, China. Cockroaches in different life cycles were identified according to their distinct body characteristics, including body size, wings, and body color. Simultaneously, 47 feedstuff samples used in this feedlot were also collected, including 24 corn flour and 23 wheat bran samples. All of the samples were transported to the laboratory immediately and stored at −4 °C until further analysis.

Cockroach samples were cleaned, freeze-dried, ground, and spiked with surrogate standards (naphthalalene-d_8, acenaphthylene-d_{10}, phenathrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}) before extracted with a mixture of 200 mL acetone: hexane (1:1, v:v) for 24 h. The extract was subjected to a gel permeation chromatography column and eluted with a mixture of dichloromethane: hexane (1:1, v:v). The fraction from 100 to 150 mL were collected and concentrated to 2 mL and then were further purified and fractionated using a glass column packed with alumina: silica gel (6:12, v:v). The first fraction of eluent, 6 mL of hexane, was discarded. The second fraction, 70 mL of hexane and dichloromethane (7:3, v:v), which contained most of the target compounds, was collected. This eluent was concentrated by rotary evaporation and further reduced under a gentle N_2 stream to a final volume of 500 μL. A known amount of internal standards (2-fluorobiphenyl and p-terpheny-d_{14}) was added prior to instrumental analysis. Feedstuff samples were subjected to the same pretreatment procedure.

2.3. Instrumental analysis and quality control

Concentrations of target analytes were determined using gas chromatography and mass spectrometry (GC–MS, Agilent 7890 A GC equipped with 5975 C MSD; Agilent Technologies, Foster City, CA) with a splitless injection. Gas chromatographic separation was accomplished using a 30 m DB-5MS fused silica capillary column (0.25 mm i.d., and 0.25 μm film thickness; J&W Scientific, Folsom, CA). High purity helium was used as the carrier gas. The mass selective detector was operated in the selected ion monitoring. The column oven temperature was initially programmed from 60 °C to 200 °C at 10 °C/min, from 200 °C to 214 °C at 2 °C/min, then from 214 °C to 254 °C at 5 °C/min (held for 2 min), and finally from 254 °C to 290 °C at 18 °C/min (held for 17 min).

Procedural blank and spiked blank samples were processed with each batch of 10 samples to monitor procedural contamination. Recoveries of the surrogate standards spiked into cockroach samples were $68 \pm 21\%$, $76 \pm 15\%$, $83 \pm 20\%$, $117 \pm 13\%$, and $91 \pm 23\%$ for naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}, respectively. These recoveries in feedstuff samples were $64 \pm 12\%$, $86 \pm 18\%$, $89 \pm 17\%$, $114 \pm 21\%$, and $93 \pm 14\%$ for naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}, respectively. The concentrations of the analytes were determined with an internal calibration curve. The lowest concentration level from the calibration curve was defined as the reporting limit. Only little amount of target analytes were found in procedural blank samples but lower than the reporting limit. The concentrations of target compounds in the current study were presented on a dry weight basis. Reported concentrations were not corrected with the recoveries of the surrogate standards.

2.4. Statistical analyzes

Differences between mean concentrations of PAHs and HPAHs in young nymphs, old nymphs, and adults were examined by One-Way Analysis of Variance (One-Way ANOVA) using "SPSS 16.0 for Windows". Nonparametric Spearman's correlation analysis was performed to examine the relationships between mean concentrations of PAHs and HPAHs in cockroaches and feedstuff. Kolmogorov–Smirnov test was applied to the data distribution analysis.

3. Results and discussion

3.1. PAHs and HPAHs in cockroach and feedstuff

The mean, median, minimum, and maximum concentrations of PAHs and HPAHs in cockroach and feedstuff samples were summarized in the Supplementary Material (Table S1). Concentrations of Σ_{16}PAHs in young nymphs, old nymphs, and adults ranged from 162 to 1025, 252 to 967, and 267 to 1168 ng/g, respectively. The mean concentration of Σ_{16}PAHs in old nymphs was 586 ng/g, followed by 557 ng/g in adults, and 473 ng/g in young nymphs. As for feedstuff samples, levels of Σ_{16}PAHs ranged from 178 to 312 ng/g (mean, 242 ng/g) in corn flour and 77.2 to 176 ng/g (mean, 119 ng/g) in wheat bran. Among individual PAHs, Nap was dominant in cockroaches, accounting for 53.5%, 45.6% and 51.7% of the Σ_{16}PAHs in young nymphs, old nymphs, and adults, respectively, whereas Phe was dominant in feedstuffs, accounting for 14.9%, and 25.9% of the Σ_{16}PAHs in corn flour and wheat bran, respectively. Generally, Nap, Phe, Flu, and Pyr were the main PAH individuals in all of the cockroach samples with an order Nap > Phe > Flu > Pyr. Also, these four compounds were the dominant PAH individuals for feedstuffs. No significant difference between mean concentrations of individual PAHs in young nymphs, old nymphs, and