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Characteristics and potential health risk of rural Tibetans' exposure to polycyclic aromatic hydrocarbons during summer period

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ABSTRACT

Biomass fuels remain main energy sources in many remote rural regions, but potential health hazards from exposure to biomass combustion fumes have not been adequately assessed. Combustion of biomass fuels generates abundant polycyclic aromatic hydrocarbons (PAHs); hence residential exposure to PAHs can be used to evaluate the potential health risk to remote rural populations. The present study selected rural Tibetans to address the above-mentioned issue. Samples of indoor air and dust, human urine and local foods (Tsampa flour and buttered tea) were collected from five rural households in Langkazi County, an agricultural and pasturing region in Tibet of China in the summer season, which represented the best-case scenario as no heating was required. Residential exposure to PAHs by adults amounted to benzo[*a*]pyrene equivalent (BaP_{eq}) dosages of 110–760, 1.2–50 and 0.5–23 ng d^{-1} for ingestion, inhalation and dermal contact, respectively. Daily intakes of naphthalene, fluorene, phenanthrene and pyrene estimated from urinary monohydroxy PAH metabolites and from diet and inhalation exposure to PAHs were comparable (3.9, 1.9, 12 and 3.3 μg d^{-1} versus 9.5, 2.5, 5.1 and 1.1 μg d^{-1}), indicating the utility of external exposure in assessing daily intake of PAHs. The median incremental lifetime cancer risk was 32×10^{-6} (95% confidence interval: 0.7–73 $\times 10^{-6}$) for ingestion and 2.4×10^{-6} (95% confidence interval: 0.02–12 $\times 10^{-6}$) for inhalation and dermal contact combined, indicating moderate to slight potential cancer risk. Diet is the dominant source of health hazards for rural Tibetans, but cooking fumes also present a meaningful concern. The present study demonstrates that the pristine lifestyles of remote rural residents may be of global health concern, and merit further investigations.

1. Introduction

Biomass fuel is used by almost 3 billion people around the globe as the main source of domestic energy (IEA, 2014), due to limited access to newer types of energy (Guta, 2014). For example, solid biomass is believed to account for over 89% of the daily energy use in Ethiopia (Guta, 2012) and > 90% of domestic energy is solid biomass fuel such as fuel wood and dry dung cake in Tibet, China (CNBS, 2002). The relatively pristine lifestyle of rural households of Nepal and Tibet relies on biomass fuel for cooking and/or heating, largely within indoor settings (Gao et al., 2009). Biomass combustion for cooking and heating exposes people to increased concentrations of contaminants, such as particulate matter and gases, up to 10–20 times higher than outdoor concentrations (Hu et al., 2016). Many remote rural regions are distant from industries and traffic (Goldsmith, 2008; Yang et al., 2013), cooking and heating are expected to be the prevailing sources of indoor air pollution. Available literature however has largely overlooked the issue of health risk to remote rural populations from exposure to this form of environmental contamination.

Biomass fuel combustion has long been recognized to generate abundant polycyclic aromatic hydrocarbons (PAHs), which are genotoxic and carcinogenic to humans (Abdullahi et al., 2013; Li et al., 1994; Seea and Balasubramaniana, 2006), in addition to particulate matter, nitrogen oxides, carbon monoxide and sulfur dioxide (Ge et al., 2004). Numerous studies have identified PAHs as the dominant contributors to potential human health risk (Liu et al., 2014; Liu et al., 2012) in various environmental settings of China, e.g., urban areas (Yu et al., 2015), rural residency (Chen et al., 2015; Shen et al., 2014) and e-waste recycling zones (Luo et al., 2015) compared to other organic contaminants such as halogenated and organophosphate flame retardants, even in urban indoor environments. As one of the most remote regions, atmospheric pollutants in Tibet have been seriously

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investigated, but most studies mainly focused on toxic elements, $PM_{2.5}$ and CO (Kang et al., 2009; Li et al., 2012b). Therefore, it is reasonable to use residential exposure to PAHs in assessing the potential health risk to the population residing in remote rural regions.

To address the above-mentioned knowledge gap, we used rural Tibet Autonomous Region as a case study and assessed the potential health risks for rural Tibetans' exposure to PAHs generated from different sources, such as combustion of biomass fuels and foods. Besides inhalation and dermal contact, dietary intake was also examined in the present study for comparison as it has been demonstrated to be the dominant route of exposure to PAHs (Chen et al., 2015; Ma and Harrad, 2015; Suzuki and Yoshinaga, 2007). Samples of suspended particulate matter, gaseous phase, indoor dust, local foods (Tsampa flour and buttered tea; Supplementary data Text S1; "S" designates text, tables and figure in the Supplementary data thereafter) and residents' urine were collected. All samples except urine were analyzed for PAHs, while urine samples were processed for monohydroxy PAH metabolites (OH-PAHs), biomarkers for internal exposure to PAHs (Jongeneelen et al., 1985). Based on these measurements, we estimated the daily uptake of PAHs by rural Tibetans via inhalation, dermal contact and dietary consumption and assessed the potential health risk related to exposure scenarios. The results from the present study are expected to provide some baseline information for stimulating further investigations into the potential health risk of remote rural populations around the world, as these populations mostly lead a similar pristine lifestyle as the rural Tibetans.

2. Materials and methods

2.1. Materials

All calibration standards for target analytes, as well as internal and surrogate standards, and materials used in the present study are described in detail in Text S2.

2.2. Sample collection

Sampling was conducted on August 8–29, 2015 at rural Tibetan households located in Langkazi County (Fig. 1), an agricultural and pasturing region in Tibet Autonomous Region of China located at an altitude of 4400 m with a per capita gross domestic product of 12,000 RMB ($1750 USD). It well represents a remote rural population with a pristine lifestyle and with minimal influences of industrialization and urbanization. Target residences were selected randomly because the residences in this region have similar architecture styles and comparable air ventilation conditions (Fig. 1). During the sampling period, residents' daily schedules were not disrupted and yak dung was not used for heating in the evening but used only for cooking. Daily cooking and other activities were conducted inside the integrated room in each household. Most local residents used the same type of cast iron stove with chimney for cooking and heating. A second sampling was planned in the winter season, but was abandoned as we failed to secure willing participants. Because no heating is required in summer, exposure to cooking fume only represents the best-case scenario.

Also due to the difficulty in securing willing participants, only five households were selected for collection of air, indoor dust, food and urine samples. In non-smoking residences, gaseous and particle samples were collected with QCD-3000 air samplers (Yancheng Galaxy Science and Technology, China) in outdoor, kitchen, bedroom and living room (at ~1 m above the ground) at different time points, representative of different exposure scenarios. Polyurethane foam and 47 mm diameter glass microfiber filters (Whatman International, Maidstone, England) were used to collect gaseous and particle samples, respectively. Sampling was conducted daily for two days during 11:00–13:00 (cooking time) and 13:00–11:00 next day (non-cooking time). Tsampa flour and butter tea samples were collected from five households. Indoor dust samples were also collected from kitchens, bedrooms, living rooms and blankets. In addition, urine samples were collected during 7:00–8:00 and 18:00–19:00 from 18 local residents. Demographic groups are divided into children (1–11 years old), adolescents (12–17 years old) and adults (> 17 years old). Detailed information is presented in Table S1. Overall, 30 air and particle samples (300 and 3300 L during cooking and non-cooking periods, respectively), 15 indoor dust (from 1 m^2), 10 food (30 g for Tsampa flour and 20 mL for Butter tea) and 36 urine (3 mL) samples were collected.

2.3. Sample extraction and instrumental analysis

The detailed extraction and cleanup procedures for food and air samples can be found elsewhere (Wu et al., 2015). All samples were spiked with the surrogate standards before extraction. Gaseous, Tsampa flour and indoor dust samples were Soxhlet extracted for 48 h with a mixed solvent of hexane, dichloromethane and acetone (2:2:1 in volume). Particle samples were sonicated with 15 mL of the mixed solvent mentioned above. Butter tea samples were shaken with 20 mL of the mixed solvent. Each extract was concentrated and solvent-exchanged to hexane, and concentrated again to 0.1 mL. Before instrumental analysis, each extract was spiked with the internal standards. The final concentration of the surrogate and internal standards was 1.0 μg mL^{-1}. The correlation coefficient of calibration curve were > 0.995. Bio-Beads SX-3 was used to purify food samples for removing lipid before being concentrated to 1.0 mL.

A Shimadzu gas chromatograph–mass spectrometer (GCMS-2010 Plus) was used to analyze all samples. An HP-5MS capillary column (30 m × 0.25 mm with a 0.25 μm film thickness) was used for chromatographic separation. The column temperature was set initially at 60 °C (held for 1 min) and elevated to 250 °C at 20 °C min^{-1}, ramped to 280 °C at 5 °C min^{-1} (held for 2 min), and further increased to 300 °C at 20 °C min^{-1} (held for 15 min). All samples were injected (1 μL each) automatically in a temperature vaporizer programmed with an original temperature of 60 °C and elevated to 250 °C at 400 °C min^{-1}. Ultrahigh-purity helium was used as the carrier gas with a flow rate of 1 mL min^{-1}. The ion source temperature was 250 °C.

Urine samples were prepared following a previously reported procedure (Fan et al., 2012) with minor modifications. Briefly, 2 mL of urine sample was spiked with 10 μL of the surrogate standards (50 ng of 1-hydroxynaphthalene-d_7; 10 ng of 1-hydroxyphenanthrene-d_9 and 10 ng of 1-hydroxypyrene-d_9), and then 1 mL ammonium acetate buffer (1 M, pH = 6.5) and 50 μL β-glucuronidase (200 units mL^{-1}) for incubation at 37 °C overnight. Each hydrolyzed sample was subject to solid phase extraction with a C18 cartridge, which was preprocessed with 5 mL of methanol and water and 10 mL of monopotassium phosphate buffer (25.0 μmol L^{-1}). The flow rate was maintained at < 1 mL min^{-1}. The loaded cartridge was washed with 4 mL of monopotassium phosphate buffer (25.0 μmol L^{-1}) and 5 mL of water to remove matrix interferences. The cartridge was dried completely and eluted with 10 mL of methanol. The extract containing the target analytes was concentrated to 500 μL under a mild stream of nitrogen. The concentrated extract was filtered through a nylon filter (0.22 μm) and spiked with the internal standards before instrumental analysis.

All urine sample extracts were analyzed with a Shimadzu DGU-30A LC interfaced with an AB SCIEX TRIPLE QUAD™ 5500 MS system. An Agilent Zorbax Eclipse Plus C18 column (2.1 × 100 mm, 1.8 μm) was used for chromatographic separation. The mobile phases were 40% methanol in water (v/v; solvent A) and methanol (solvent B). The gradient elution program was as follows: 0–3 min, 5% solvent B; 3–5 min, 30% solvent B; 5–10 min, 30% solvent B; 10–15 min, 40% solvent B; 15–16 min, 80% solvent B; 16–20 min, 70% solvent B; 20–21 min, 5% solvent B. Each extract of 5 μL was injected by an autosampler into the chromatographic column at a temperature of 40 °C and a flow rate of 0.27 mL min^{-1}. Mass spectra were acquired in the multiple reaction-monitoring mode with an ion spray voltage of 4500 V