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Winter air pollution by and inhalation exposure to nitrated and oxygenated PAHs in rural Shanxi, north China

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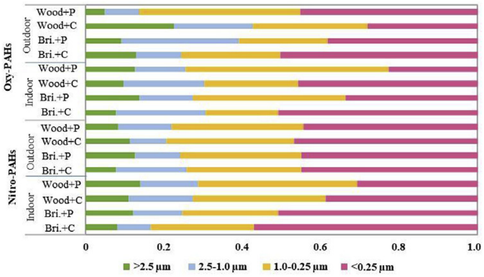
GRAPHICAL ABSTRACT



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ABSTRACT

Polar polycyclic aromatic hydrocarbons (PAHs) derivatives like nitrated and oxygenated PAHs have higher toxic potentials than the parent one, and are receiving growing interests. In this study, we investigated household air pollution and personal exposure to nitro- and oxy-PAHs during a winter period in rural Shanxi, northern China. The overall arithmetic means of 24-h average indoor nitro-PAHs and oxy-PAHs were 10.2 ± 3.6 and 76.8 ± 51.8 ng/m^3, respectively, that were much higher than the 7.98 ± 4.30 and 54.7 ± 45.4 ng/m^3 in the outdoor air. Nearly 90% of particulate PAHs derivatives were enriched in fine $PM_{2.5}$ and even finer $PM_{1.0}$ fraction. Daily inhalation exposure to nitro- and oxy-PAHs for the rural population were 8.41 ± 3.08 and 68.5 ± 79.7 ng/m^3, respectively. Residents burning briquette for cooking were found to have lower household air pollution and exposure levels compared with those burning wood. The calculated time-weighted average concentration overestimated, though correlated positively, the daily inhalation exposure compared to the that from personal carried samplers.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs), mainly produced from incomplete combustion process (Shen et al., 2013a,b), are of worldwide concerns due to their carcinogenic and mutagenic potentials (Delgado-Saborit et al., 2011; Chakravarti et al., 2008; Boström et al., 2002; Mohammed et al., 2016). Ubiquitous PAHs contamination in environment has been investigated extensively in both developed (Alves et al., 2017; Mishra et al., 2016) and developing countries (Duan et al., 2014Hoseini et al., 2016; Vaio et al., 2016; Li et al., 2016a,b; Huang et al., 2014a). Besides parent PAHs, PAH derivatives such as nitro-PAHs and oxy-PAHs are receiving growing interest as they may have higher

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toxic potentials compared to the corresponding parent ones (IRAC, 2016; Albinet et al., 2008; OEHHA, 2011). PAH derivatives could be formed by photochemical reactions of parent-PAHs with atmospheric oxidants (OH, O_3, NOx) (Bandowe and Meusel, 2017; Jariyasopit et al., 2014; Zimmermann et al., 2013), and/or directly from primary combustion emissions (Shen et al., 2013a; Huang et al., 2014b).

In a few past studies, contamination and orignis of nitro- and oxy-PAHs in ambient air in China were investigated (Li et al., 2015; Bandowe et al., 2014; Tang et al., 2017; Zhuo et al., 2017). Those studies, of which most were in large or mega-cities, provided important information on characteristics (pollution levels, phase and size distribution, sources, etc.) and adverse health impacts of the derivatives, whereas PAHs derivatives contamination in rural area has been rarely characterized (Ding et al., 2012; Shen et al., 2016; Chen et al., 2017). Though detailed inventories of these derivatives are still not available, the extensive use of solid fuels is believed to be an important source of these derivatives, particularly during cold seasons (Lin et al., 2015a, 2015b). A previous study in northern China Plain found that ambient nitro-PAHs and oxy-PAHs in rural villages could be comparable, or even higher than, those in the urban area (Li et al., 2015).

In this study, a field campaign was conducted to investigate household air pollution (HAP) and inhalation exposure to nitro- and oxy-PAHs in rural Shanxi, north China, during a winter period. Both gaseous and particulate phases were sampled. Size-segregated particles with a diameter < 0.25, 0.25–1.0, 1.0–2.5 and $> 2.5\,\mu m$ were collected to determine the size distribution. The personal inhalation exposure to nitro-PAH and oxy-PAHs was quantified by using portable samplers, and compared to the results calculated from the area concentration. To our knowledge, rural air pollution by PAHs derivatives, particularly with detailed size distribution information, and inhalation exposure assessment by adopting portable samplers is scarce. The study is expected to improve our understanding on the occurrence and health impacts of these polar derivatives in rural China.

2. Method

2.1. Field study site and sampling

The field campaign was conducted in rural Taigu county, Shanxi province in winter (January 2015) with an average ambient temperature of approximately $-12\,^{\circ}C$. Solid fuels such as peat and coal were often burnt in individual homes for heating. The typical cooking fuels were briquettes and wood (Du et al., 2017).

Portable and stationary samplers were used to investigate personal exposure and household air pollution, respectively. The sampler is comprised of a Sioutas cascade impactor pump (SKC, Eighty Four, PA, USA, flow rate at 8.2 L/min) coupled with four stage impactors ($< 0.25\,\mu m$, 0.25–1.0 μm, 1.0–2.5 μm, and $> 2.5\,\mu m$). The glass fiber filters (GFFs, 0.45 μm, BUCK, Orlando, FI, USA) and a low-density polyurethane foam cartridge (PUFs, 22 mm diameter × 7.6 cm) were used to simultaneously collect size-segregated particle and gaseous phase nitro- and oxy-PAHs. All filters were pre-baked at 450 °C for 6 h and equilibrated in a desiccator in the laboratory. The filters were packed and sealed separately in clean aluminum foil bags before and after each sampling cycle.

Paired indoor and outdoor air were sampled from households randomly selected in the villages. The stationary indoor samplers were placed about 1.5 m above the ground and at least 1.0 m from the wall and the stove, and the corresponding outdoor samplers were placed in the front yard of the houses. A minimum of 1.0 m is an empirically principal approach to measure indoor air pollution (Wu et al., 2015a), and could be adjusted slightly according to the real setting and sampling conditions of the kitchen (Fischer and Koshland, 2007). One adult inhabitant of each household was asked to carry a personal sampler during the one-day measurement period. Participators were asked to carry samplers for a duration of 24 h, and when sleeping or using the restroom, the sampler should be placed nearby within 1.0 m. A written informed consent was signed by individual volunteer and their personal information (gender and age) and life style (fuels/stoves used in the households, whether they were primary cookers, etc.) were recorded in survey questionnaires. A total of thirty-five households participated in this measurement, of which 5 stationary samples and 7 personal samples were discarded due to technical problems for instance unexpected sampling stop. Finally, 30 indoor samples, 30 outdoor samples and 28 personal exposure samples were used for further analysis (Table S1). The field campaign was finished in a week with very similar weather conditions (Table S2).

2.2. Laboratory analysis

Following the analysis procedure in our previous studies (Chen et al., 2017; Shen et al., 2012), the GFFs were extracted with 25 mL of a n-hexane/acetone (1:1, V/V) mixture using a microwave accelerated extraction system (CEM, Mars Xpress, USA). The temperature was increased to 110 °C in 10 min and was then kept constant for 10 min at 1200 W. The PUFs were Soxhlet extracted for 8 h with 150 mL of the same mixture as the GFFs. After extraction, the solvent was concentrated to about 1 ml using a rotary evaporator (N-1100; EYELA, Bunkyo-ku Tokyo, Japan). Then, the solvent was transferred to a silica/alumina column for purification. The column was conditioned with 20 mL hexane (discarded) and then 70 mL hexane/dichloromethane mixture (1:1, v/v), which was collected, concentrated to ~1 mL and spiked with deuterated internal standards (1-nitroanthracene-d9 and 1-nitropyrene-d9, J&W Scientific, USA). Concentrations of the target compounds were quantified with a gas chromatograph coupled with a mass spectrometer (GC-MS, Agilent 6890/5973, Santa Clara, CA, USA) using the NCI mode. A DB-5MS capillary column (0.25 mm i.d. 9 × 30 m, 0.25 μm film thickness), high-purity helium as carrier gas and methane as reagent gas. All the derivative PAHs were identified based on retention times and qualitative ions of the standards (J&W Chemical, Newark, DE, USA). The temperature program of GC-MS was the same with a previous study (Zhuo et al., 2017). Twelve nitro-PAHs and four oxy-PAHs were quantified (Table S3).

2.3. Quality control and data analysis

Procedure and reagent blanks were measured and the values were subtracted from the sample results. All samples were stored in a refrigerator at a temperature of $-20\,^{\circ}C$ before lab analysis. The PUFs were also pre-cleaned using dichloromethane, n-hexane and acetone for 8 h, respectively, using the Soxhlet extraction method. Detection limits and recoveries of target PAHs derivatives were determined in preliminary experiments by spiking authentic standards on sampling media (Shen et al., 2012; Li et al., 2015; Zhuo et al., 2017). Recoveries of the spiked standards were 92–138% and 70–108% for PUFs and GFFs, respectively. Recoveries of the surrogate (1-Br-2-Nitrobenzene, J &W Chemical, USA), which was randomly added into 20% samples, for gaseous and filter samples were 83–108% and 72–94%, respectively. The recovery of surrogate was not applied to correct the measured pollutant concentration but instead to monitor the quality of laboratory analysis. Statistical analysis was performed using SPSS 21.0 (IBM Corporation, Armonk, NY, USA) at a significance level of 0.05. The BaPeq (BaP equivalent concentration) was calculated according to following equation (Bandowe et al., 2014):

$$BaPeq = \sum_{i=1}^{i=n} Ci \times TEFi$$

where Ci = concentration of nitro-PAH congener i; TEFi = the toxicity equivalency factor (TEF) of nitro-PAH congener i. The TEF of individual nitro-PAH was listed in Table S3.