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Biomass burning contributed most to the human cancer risk exposed to the soil-bound PAHs from Chengdu Economic Region, western China

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ABSTRACT

The purpose of this study was to assess the human cancer risk due to the exposure to the soil-bound polycyclic aromatic hydrocarbons (PAHs) from Chengdu Economic Region (CER), western China with the main concern on cancer risk source apportionment. The total concentrations of sixteen PAHs ranged from 12.5 to 75431 ng g^{-1}, with a mean value of 3106 ng g^{-1}, which suggested that the most areas of CER were contaminated. Source apportionment of PAHs was conducted by the positive matrix factorization (PMF) model and the biomass burning contributed most (63.6%) to the total PAHs, followed by petroleum combustion (16.0%), coke source (11.3%), and petrogenic source (9.2%). Results from incremental lifetime cancer risk (ILCR) calculation showed that soil ingestion exerted the highest cancer risk (accounted for 98.1 − 99.3% of the total cancer risk) on human health among three different exposure pathways, followed by dermal contact (0.66 – 1.83%) and inhalation (0.03 – 0.04%). Among different age groups, adult suffered the highest cancer risk via any exposure pathways. Based on PMF and ILCR methods, the cancer risk source apportionment was conducted and the biomass burning showed moderate cancer risk. The petrogenic, coke, and petroleum sources showed low cancer risks to human. To analyze the sensitivity of the parameters used in ILCR calculation, Monte Carlo simulation was employed. The results indicated that the contribution of each source and exposure duration (ED) were the influential parameters on human health associated with soil-bound PAHs. Therefore, much attentions should be paid to biomass burning to avoid cumulative cancer risk.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are widespread pollutants in the environment, which are carcinogenic and mutagenic to human (Nisbet and LaGoy, 1992; Durant et al., 1996). Sixteen PAHs including naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fl), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benz[*a*]anthracene (BaA), chrysene (Chr), benzo [b] fluoranthene (BbF), benzo [k] fluoranthene (BkF), benzo [a] pyrene (BaP), indeno [1,2,3-cd] pyrene (IcdP), dibenz [a, h] anthracene (DBA), and benzo [ghi] perylene (BghiP) were listed as the priority pollutants by the United State Environment Protection Agency (USEPA) (USEPA, 2003). Seven of them, namely Chr, BaA, BbF, BkF, BaP, IcdP, and DBA were received much attention due to their potential carcinogenic and mutagenic characteristics (IARC, 1986). PAHs are emitted into the environment by anthropogenic activities such as combustion processes or the pyrolysis of fossil fuels (Chang et al., 2006).

Several models have been applied to assess the risk of PAHs including risk quotient (RQ) (Zheng et al., 2016), BaP equivalent (BaPE) (Zhang et al., 2012), toxic equivalent quantity (TEQ_{BaP}), and incremental life cancer risk (ILCR) (Peng et al., 2011). These models calculate the PAH risks in different matrixes (i.e., soil, sediment, and particle) based on the total PAH concentrations or BaP TEQ concentrations. However, PAHs from different sources may exhibited different risk levels. It is significant to figure out the risks of various PAH sources before the cost-effective abatement strategies are developed. Therefore, the combination of these risk assessment models and receptor models are developed to allocate the risks of different PAH sources. For example, Zhang et al. (2012) and Xu et al. (2014) employed the Unmix and BaP equivalent (BaPE) to calculate the contribution of each PAH source to the total risks in sediment. Tian et al. (2014) and Lang et al. (2015) also used the positive matrix factorization (PMF) to assess the contribution of different sources to the carcinogenic potencies. The combination of chemical mass balance (CMB) and

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TEQ_{BaP} was also reported to the source apportionment of PAH risks (Li et al., 2014a). These studies found that PAHs from different sources showed different risk levels with higher contributions from high-temperature combustion sources (such as gasoline and diesel engine emission) and less from petrogenic sources (Li et al., 2014a; Lang et al., 2015). However, these researches mainly focused on the ecological risk assessment of PAHs, while the study concerning the potential cancer risks of different PAH sources on human health is less studied. For example, a new receptor model (PMF-ILCR) was developed to cancer risk source apportionment of particle-bound PAHs and found that gasoline emission posed the highest cancer risk to human (Liu et al., 2015). However, the ILCR method is sensitive to several parameters such as exposure time (ET), exposure frequency (EF), body weight (BW), and skin surface area exposed (SA). These parameters were limited to a certainty or empirical values. Therefore, these exposure parameters significantly affect the ILCR results. To reduce the variability in measurements and the heterogeneity in population or exposure parameters, the Monte Carlo simulation is widely used to calculated the ILCR (Wu et al., 2011; Yang et al., 2014, 2015).

Soil is an important sink for PAHs due to their high hydrophobicity characteristic and it may allow the entry of PAHs into human through the food chains. Therefore, risk assessment of soil-bound PAHs is important. Inspired by these studies, a new method combining PMF, ILCR model, and Monte Carlo simulation was carried out to evaluate the cancer risk on human associated with soil-bound PAHs from different sources. We hypothesized that PAHs from different sources may generate different concentrations of carcinogenic PAHs to the surrounding, leading different probability of cancer risk exerted upon humans. This study aimed to the cancer risk source apportionment of soil-bound PAHs that were attributed to different PAH sources. Therefore, source apportionment of PAHs was conducted by the USEPA PMF receptor model. The contributions of different PAH sources derived from PMF model were then converted to TEQ_{BaP} concentrations. The source contributions of TEQ_{BaP} along with the ILCR model and Monte Carlo simulation were employed to evaluate the cancer risks that may be exerted on three different age groups people via three exposure pathways including soil ingestion, inhalation, and dermal contact.

2. Methods

2.1. Sample collection and PAHs analysis

As one of the largest agricultural provinces in China, the total PAH emissions in Sichuan ranked the first in China in 2003, with an average of 5.35 kg km^{-2} (Xu et al., 2006; Zhang et al., 2007). As the most developed urban agglomeration in Sichuan Basin, the Chengdu Economic Region (CER) includes six cities, namely Chengdu (CD), Deyang (DY), Leshan (LS), Mianyang (MY), Meishan (MS), and Ya'an (YA). A total of 245 soil samples were collected in the CER (Fig. S1, see supplementary materials) and the detailed sampling and analysis procedures were described elsewhere (Xing et al., 2011). Briefly, 10 g of each pretreatment soil sample was spiked with 1000 ng mixed recovery surrogates (naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, and perylene-d12). Activated copper granules were used to remove the elemental sulphur. After 24 h Soxhlet-extracted with 150 mL dichloromethane (DCM), the sample extract was concentrated and then solvent-exchanged to hexane by a rotary evaporator. A deactivated alumina/silica gel column (1:2, v/v) was used to clean up the extract and the PAH fractions were eluted with 30 mL of DCM/hexane (2:3). The target eluate was then concentrated to 0.2 mL under a high purity nitrogen stream. Prior to the analysis of PAHs, a known quantity (1000 ng) of hexamethylbenzene was spiked as an internal standard

Sixteen PAHs were measured using GC-MS (Agilent 6890 N/5975 MSD). The PAHs were separated under the highly pure helium gas (carrier gas) at a constant flow rate of 1.5 mL min^{-1} by GC equipped with a DB-5 capillary column (30 m × 0.25 mm i. d × 0.25 μm film thickness) and detected by mass detector (EI model, 70 eV) operated in selected ion monitoring (SIM) mode. The chromatographic conditions were set as follows: injector temperature 270 °C; detector temperature 280 °C; oven temperature was kept at 60 °C for 5 min and increased to 290 °C at a rate of 3 °C min^{-1} and kept at 290 °C for 40 min.

The procedural blanks, spiked blanks, and sample duplicates were deployed to quality assurance/control. The surrogate recoveries of naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, and perylene-d12 were 43 – 54%, 67 – 72%, 74 – 95.0%, 70 – 85%, and 85 – 110%, respectively. The instrument detection limits (IDLs) of 16 PAHs were in the range of 0.07 − 0.58 ng g^{-1} and more information can be found in Table S1.

2.2. PMF description

PMF model is one of three receptor models recommended by the USEPA to pollutants source apportionment. Briefly, PMF model decomposes a matrix of observed sample dataset (X) into two matrices: source contribution matrix (G) and source profile matrix (F):

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \quad (1)$$

where x_{ij} is the concentration of the jth PAH species measured in the ith soil sample; g_{ik} represents the contribution of the kth source to the ith sample; f_{kj} represents the mass fraction of the jth compound from the kth source, and e_{ij} is the residual for each sample/species. The target of PMF model is to calculate the minimum of the objective function Q considering the residuals (e_{ij}) and uncertainty (u_{ij}):

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left(\frac{e_{ij}}{u_{ij}} \right) \quad (2)$$

There are two types of uncertainty: sample-specified and equation-based. In this study, the equation-based uncertainty was introduced into PMF calculation. If the concentration is greater than method detection limit (MDL), the uncertainty is calculated according to the following equation:

$$u_{ij} = \sqrt{(error\ fraction \times concentration)^2 + (MDL)^2} \quad (3)$$

If the concentration is less than MDL, the uncertainty is estimated using the following equation:

$$u_{ij} = \frac{5}{6} \times MDL \quad (4)$$

The USEPA PMF (5.0) model was carried out in this study. Sixteen PAH species were firstly categorized into strong, weak, and bad according the signal to noise (S/N) or the percentage of samples below the MDL (BMDL). Generally, species with S/N greater than 2.0 are grouped into strong; species with S/N greater than 0.2 but less than 2.0 or with BMDL less than 50% are grouped into weak; species with S/N less than 0.2 or BMDL greater than 60% are grouped into bad and excluded from the PMF calculation (Callén et al., 2014). According to these rules, Ace was grouped into bad and excluded from the PMF model; Ace was grouped into weak and the uncertainty of this species increased by three times; and the rest species were grouped into strong. The factor number was tested from 2 to 6 and each base model was run with a random seed for 20 times. The optimum factor number was decided according to whether the ratio of Q_{true} to $Q_{exception}$ close to one. In this study, despite five- factor solution had Q_{true} to $Q_{exception}$ more closely to one, there were meaningless sources only weighted on a single species. Consequently, we considered that four-factor was the optimum solution.

The uncertainties and error estimation were estimated using the bootstrap (BS) and displacement of factor elements (DISP). The most residual scales were between − 3 and 3 and the Pearson correlation coefficients (R^2) between the observed and predicted concentrations