



Occurrence of nitro- and oxy-PAHs in agricultural soils in eastern China and excess lifetime cancer risks from human exposure through soil ingestion



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ABSTRACT

The quality of agricultural soil is vital to human health, however soil contamination is a severe problem in China. Polycyclic aromatic hydrocarbons (PAHs) have been found to be among the major soil contaminants in China. PAH derivatives could be more toxic but their measurements in soils are extremely limited. This study reports levels, spatial distributions and compositions of 11 nitrated (nPAHs) and 4 oxygenated PAHs (oPAHs) in agricultural soils covering 26 provinces in eastern China to fill the data gap. The excess lifetime cancer risk (ELCR) from the exposure to them in addition to 21 parent PAHs (pPAHs) via soil ingestion has been estimated. The mean concentration of Σ nPAHs and Σ oPAHs in agricultural soils is $50 \pm 45 \mu\text{g}/\text{kg}$ and $9 \pm 8 \mu\text{g}/\text{kg}$ respectively. Both Σ nPAHs and Σ oPAHs follow a similar spatial distribution pattern with elevated concentrations found in Liaoning, Shanxi, Henan and Guizhou. However if taking account of pPAHs, the high ELCR by soil ingestion is estimated for Shanxi, Zhejiang, Liaoning, Jiangsu and Hubei. The maximum ELCR is estimated at $\text{ca.}10^{-5}$ by both deterministic and probabilistic studies with moderate toxic equivalent factors (TEFs). If maximum TEFs available are applied, there is a 0.2% probability that the ELCR will exceed 10^{-4} in the areas covered. There is a great chance to underestimate the ELCR via soil ingestion for some regions if only the 16 priority PAHs in agricultural soils are considered. The early life exposure and burden are considered extremely important to ELCR. Emission sources are qualitatively predicted and for areas with higher ELCR such as Shanxi and Liaoning, new loadings of PAHs and derivatives are identified. This is the first large scale study on nPAHs and oPAHs contamination levels in agricultural soils in China. The risk assessment based on this underpins the policy making and is valuable for both scientists and policy makers.

1. Introduction

The agricultural land in Eastern China produces 64% of grains and 80% of vegetables, which serves 70% of Chinese population (China Ministry of Agriculture, 2014). The ‘Report on national soil pollution survey (2014)’ reveals that ca. 20% of farmland in China has pollutant levels exceeding guideline values and polycyclic aromatic hydrocarbons (PAHs) are one of the major pollutant categories (MEP and MLR, 2014). PAHs are a class of carcinogens from the incomplete combustion of organic fuels. Their derivatives such as nitrated (nPAHs) and oxygenated PAHs (oPAHs) could derive primarily from the incomplete combustion or the photochemical reaction of parent PAHs (pPAHs) and

oxidants as secondary sources (Cochran et al., 2016; Kielhorn et al., 2003). About 21–34% of 16 USEPA priority PAHs (listed in Table S1 in the Supporting information (SI)) emissions (106 Gg in 2007) in China are produced in rural areas (Shen et al., 2013a; Xu et al., 2006; Zhang et al., 2008). Human health may be highly sensitive to the contamination level of PAHs and derivatives in agricultural soils, as PAH species could be easily exposed to farmers via soil ingestion during cultivation activities, or bio-accumulated by crops and expose a wider population of potential consumers into health risks (Davis and Mirick, 2006; Man et al., 2013; Yu et al., 2011). Most rural areas in China have relatively lower economic level, incomplete infrastructures and poorer social services compared to urban areas in the same region, which

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result in higher amount of dusts and wastes around the living environment. Children in rural areas in China possibly receive less education on hygiene habits such as washing hands frequently, especially before meals. These all probably lead to higher intake levels of pPAHs and derivatives for the rural population due to greater soil ingestion rates.

Epidemiologic surveys prove that higher incidences of different cancers are associated with the occupational exposure to PAHs and the quantitative monitoring data of PAHs are primary to the investigation of the exposure and risks (ATSDR, 2009). Parental exposure to PAHs may lead to behaviour problems for children such as attention-deficit hyperactivity disorder (Mortamais et al., 2017; Perera et al., 2012; Perera et al., 2011). nPAHs and oPAHs could be potentially more threatening to human health than their pPAHs, as they are found to directly react with DNA without metabolic activation and exhibit mutagenic properties, unlike pPAHs (Lundstedt, 2003; Pedersen et al., 2004; Pitts et al., 1978). nPAHs could strongly adhere to organic contents of soils and therefore be more persistent in top soils than corresponding pPAHs due to generally higher sorption coefficients (Koc) and lower water solubility compared to the corresponding pPAHs (Kielhorn et al., 2003).

To evaluate human health risks of soil PAHs and derivatives, measurements in soils are needed. Additionally, it is essential to investigate the composition, emission sources and contributions of different PAHs species to the risk. Reports on pPAHs in soils are relatively abundant but only the 16 priority PAHs are considered in the national soil survey mentioned above or widely studied in most relevant scientific researches (Sun et al., 2017; Tao et al., 2011; Zuo et al., 2007; MEP and MLR, 2014). Measurements of soil nPAHs and oPAHs are extremely limited especially for China (Bandowe and Meusel, 2017), and the few existing gauging campaigns in China are on city/regional scales (Cai et al., 2017; Wei et al., 2015; Zhang et al., 2013). In addition, many publications focus on excess lifetime cancer risks from the inhalation exposure to PAHs for the Chinese population (Shen et al., 2014; Zhang et al., 2016; Zhang et al., 2009) but much fewer are on the exposure via soil ingestion.

In the present study, a large scale gauging campaign for nPAHs and oPAHs in agricultural soils has been conducted in 26 provinces in eastern China to fill the data gap. This study reports the occurrence, spatial distribution and composition of these species in agricultural soils and diagnoses their potential emission sources. In terms of this work and previously reported pPAHs concentrations in agricultural soil for the same sampling sites (Sun et al., 2017), average daily doses (ADD) of PAHs and derivatives and an excess lifetime cancer risk (ELCR) via soil ingestion are estimated. This could supplement the knowledge on human health risks from exposure to PAHs and derivatives through multiple exposure pathways. The burden of PAHs species during childhood stage is specifically discussed. As far as the author knows, this is the first large scale study on nPAHs and oPAHs in agricultural soils in China. Such investigation reduces the systematic uncertainty for spatial analysis caused by gauging campaigns accomplished by different research groups and also provides valuable first-hand data for risk assessments. Severe soil pollution is easily neglected by the public in China, because, unlike smog for instance, it is not directly visible. However there are growing awareness and concerns among politicians and scientists (Economist, 2017). Outputs from this study will support the management of the agricultural soil quality in China.

2. Methods and materials

2.1. Sample collection and target chemicals

82 soil samples were collected during April–May 2013 from agricultural land in 26 provinces in eastern China (SI Fig. S3) by a team in Zhejiang University (Niu et al., 2014). The analysis of PAH derivatives was completed in Peking University. In short, the overlying vegetation

was removed before sample collection. Five top soil samples (0–20 cm) were taken by a pre-cleaned scoop for each sampling site and then mixed into one composition sample and packed in a pre-cleaned aluminium foil bag. Soil samples were air-dried, ground, sieved (2 mm) and stored at -20°C until analysis. More detailed sampling methods can be found in previous studies (Niu et al., 2014; Sun et al., 2017).

The target PAH derivatives included 11 nPAHs and 4 oPAHs. The nPAHs were 1-nitro-naphthalene (1N-NAP), 2-nitro-naphthalene (2N-NAP), 5-nitro-acenaphthene (5N-ACE), 2-nitro-fluorene (2N-FLO), 3-nitro-phenanthrene (3N-PHE), 9-nitro-phenanthrene (9N-PHE), 9-nitro-anthracene (9N-ANT), 3-nitro-fluoranthene (3N-FLA), 1-nitro-pyrene (1N-PYR), 7-nitro-benzo[*a*]anthracene (7N-BaA) and 6-nitro-chrysene (6N-CHR). Additionally the oPAHs were 9-fluorenone (9FO), anthracene-9,10-dione (ATQ), benzo[*a*]anthracene-7,12-dione (BaAQ) and benzanthrone (BZO). The 21 pPAHs (Sun et al., 2017) included in the risk assessment and their abbreviations are in SI Table S1.

2.2. Sample extraction, analysis and quality control

The extraction and the cleanup methods reported by previous studies (Li et al., 2016) were adopted for analysis of nPAHs and oPAHs in soils. Briefly, ca. 8 g soil packed in a glass fibre filter (GFF) were extracted by 25 mL hexane/acetone (1:1, v/v) solution using a microwave accelerated reaction system (CEM MARSXpress, NC, USA) for 20 min. The procedure temperature was raised to 110°C in the first 10 min and held afterwards. The extract was concentrated to 1 mL before being purified by a silica gel/alumina column (12 cm alumina, 12 cm silica gel and 1 cm anhydrous sodium sulfate were added into the column in sequence). 20 mL hexane was added into the column for pre-elution (discarded) followed by 50 mL hexane/dichloromethane mixed solution (1:1, v/v) for eluting nPAHs and oPAHs, which was collected. The eluate was evaporated to 1 mL and solvent-exchange to hexane, which was ultimately concentrated to 1 mL. 1-nitroanthracene-*d*₉ and 1-nitropyrene-*d*₉ were spiked as internal standard (J & W Chemicals, USA).

nPAHs and oPAHs were analysed by GC–MS (Agilent 5973 GC, Agilent 5975 MS) with a HP-5 MS capillary column in negative chemical ionization mode using the selected ion monitoring. The carrier gas and the reagent gas were high-purity helium and methane respectively. The oven temperature of the gas chromatograph was set to rise from 60°C to 150°C at a rate of $15^{\circ}\text{C}/\text{min}$ and then to 300°C at a rate of $5^{\circ}\text{C}/\text{min}$, and remain for 15 min. The individual PAH derivatives were quantified based on the retention time. Procedural and reagent blanks were analysed with the samples concomitantly. All reagents and solutions used in the purification above were of chromatographic purity. Duplicate samples were measured. The recoveries of the spiked standards of individual PAH derivatives ranged 80–133% (SI Table S3). All concentrations reported here were blank- but not recovery-corrected and are given on a dry weight basis.

2.3. Estimates of excess lifetime cancer risk by soil ingestion

A chemical-specific approach was adopted officially by US EPA and Health Canada, and also widely used in scientific researches to probabilistically estimate the ELCR from exposure to PAHs via soil ingestion (Health Canada, 2010; Lemieux et al., 2015; USEPA, 2017; Williams et al., 2013). This method employed concentrations of contaminants, body weights, exposure factors, soil ingestion rates and the oral slope factor. Concentrations of individual PAHs and derivatives were converted to BaP_{eq} (BaP equivalent concentration) by the toxicity equivalency factor (TEF) for the calculation. As a result of the uncertainty of TEF, a comprehensive review into TEF values for these chemicals was conducted with the aim to include the possible range of TEFs (Table S1). Because of the lack of TEF values for most PAH derivatives, only those with available TEFs (see SI Table S1, 27 PAHs and derivatives in total) were included in the risk estimation. The Average Daily Dose

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