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# Urbanization-Related Changes Over the Last 20 Years in Occurrence, Sources and Human Health Risks of Soil PAHs in Rural Tianjin, China

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# Abstract

Polycyclic aromatic hydrocarbons (PAHs), one of the key pollutants in urban areas, have presented a great risk to the resident health. So far, however, studies in-depth on changes of local PAH emissions and associated health risks closely related to urbanization are scarce. Here, the concentrations of PAHs were determined in 57 surface soil samples obtained from two rural districts in 2018 in Tianjin, China. The sources, risks and the linkage between urbanization and PAH contamination of soil PAHs in 2018 were compared with the data in 2001 from a previous study to investigate the changes related to urbanization effects. The temporal changes in the concentrations and composition of PAHs for two districts were similar. The increased total concentrations of soil PAHs could be attributed to the fact that ANT and DahA became the dominated compounds, which was related to changes of the PAH sources. Results of the positive matrix factorization model suggest that the major sources of soil PAHs changed from coal combustion (32.9%), petroleum sources (32.1%), and traffic sources (22.1%) in 2001 to traffic sources (63.7%) and petroleum and biomass combustion (18.7%) in 2018. Results from incremental lifetime cancer risk (ILCR) model showed that the carcinogenic risk of soil PAHs to residents also increased from safe level to low level, and dermal contact was the prevailing pathway of PAH exposure. The increase in cancer risks were mainly related to the alterations of PAH sources.

# Introduction

Polycyclic aromatic hydrocarbons (PAHs), a class of ubiquitous environmental organic contaminants, primarily stem from anthropogenic sources such as oil spills, vehicle emissions, fossil fuel and biomass combustion, industrial processes, as well as chemical manufacturing, and also from natural movements such as volcanic activity, forest fires, and diagenesis (Nisbet and Lagoy, 1992; Wang et al., 2013a). PAHs have been widely concerned owing to their ubiquitous environmental occurrences, bioaccumulation, and potential adverse effects to human (Santodonato et al., 1981). 16 PAHs has been proposed as priority pollutants by the United States Environmental Protection Agency (US EPA) (Harvey, 1991). Among these components, low molecular weight (LMW) PAHs with two or three aromatic rings are considered non-carcinogenic, while seven high molecular weight (HMW) PAHs containing 4 to 6 rings are classified as carcinogenic congeners (Waqas et al., 2014). Once released into the environment, PAHs may undergo transportation over long distances through water and air and thus remain globally in soils, sediments, waters, and atmospheres (Daskalakis and O'Connor, 1995; Manariotis et al., 2011). PAHs are resistant to degradation and prone to be absorbed by soil particles (Wang et al., 2017; Wilcke, 2007), which makes soils capable to be an important "PAH sink", burying more than 90% of the environmental PAH loads (Hu et al., 2013b; Wild and Jones, 1995).

In general, the major cause of global PAH pollution is massive emissions from human activities related to urbanization (Harrison et al., 1996), although there are some non-anthropogenic PAH sources. Many developing countries, especially China, have been currently in a changeover period between the rise of urbanization and rapid development. Due to massive urbanization and industrialization, urban areas are densely populated and are accompanied by several phenomena such as population agglomeration, increased construction of industrial facilities, and surge of vehicle use, concurrently producing large amounts of PAHs transported into urban soils by atmospheric deposition (Bozlaker et al., 2008; Dickhut et al., 2000). Additionally, PAH distribution in urban soils is primarily attributed to the type and location of their sources (Liu et al., 2010; Peng et al., 2016b). Therefore, the intensified human activities related to urban development may alter the compositions and distribution of PAHs. And these alterations probably induce additional human health risks due to different components having widely varying toxicities, which has attracted little concern to date (Cao et al., 2017).

Urbanization is likely a key factor affecting the environmental behaviors of PAHs in urban soils (Wu et al., 2019). Wang et al. (2018) proposed that population density was one of the key factors for PAH levels in urban soils from Nanjing by investigating the correlations between PAH concentrations, factors related to urbanization, and soil properties. On the basis of soil PAH concentrations of a rapidly developing town in Southern Jiangsu in 2009 and 2014, Cao et al. (2017) ascribed the changes in levels, compositions, and sources of PAHs to urbanization process. Jensen et al. (Jensen et al., 2007) reported that PAH concentrations were higher in the more-populated and urbanized areas near Oslo in southern Norway than in the less-populated areas located in northern Norway. Moreover, sediment cores obtained from lakes and reservoirs and soil samples with different stages of urbanization or collected from different depths were also introduced to identify the relationships between environmental behaviors of PAHs and urbanization process (Liu et al., 2010; Ni et al., 2011; Van Metre et al., 2000). Yet there are still few studies concerned on characterizing the influences of urbanization process on PAH concentrations, sources and health risks in urban soils within a certain period of time.

In this study, soil samples from two rural districts of Tianjin in 2018 were investigated for 16 US EPA priority PAHs to study their sources and cancer risks to local residents. Furthermore, the source apportionment and risk assessment of soil PAHs in the same areas in 2001 based on the data from a previous study (Wang et al., 2003; Zuo et al., 2007) were also introduced here to reveal the changes of emission sources and the concurrent variations as well as cancer risks during the past 20-year urbanization.

## **Material And Methods**

### Sample collection

As an important industrial city in Northern China, Tianjin is located at about 120 km east of Beijing and at the west of Bohai Bay. Jizhou district is located at 115 km north of Tianjin City and adjacent to Hebei province, with an area of 1590 km<sup>2</sup> and a population of about 900,000. From 2004 to 2016, the number of Jizhou GDP increased by 500%. The tourism revenue of Jizhou district was up to 11 billion in 2016. Ninghe district, with a population of about 400,000, is located in the east of Tianjin and close to Tianjin coastal new region, covering an area of about 1300 km<sup>2</sup>. From 2009 to 2018, the Ninghe GDP grew about 230%. A total of 57 surface soil samples (0-10 cm) from Jizhou district and Ninghe district were collected by a

stainless-steel spade in 2018 (Fig. 1a), and they were subsequently kept in dark glass bottles and transported to laboratory. All samples were naturally dried at room temperature, then sieved through a 70-mesh sieve, and finally stored at 4 °C and dark conditions prior to analysis. The sampling map of those 33 soil samples (0-10cm) from the same areas in 2001 was shown in Fig. 1b.

#### Analysis of PAHs

Sample extraction, cleanup, and instrumental conditions for PAHs followed our previous study (Shi et al., 2021). Soil samples were extracted in an accelerated solvent extraction, cleaned by a standard silica/aluminum gel column, and then concentrated prior to gas chromatography/mass selective detector analysis. A detailed description of the methods is provided in the Supplementary Content.

#### Quality assurance and quality control

Matrix-spiked recoveries, duplicates, and method blanks were processed and analyzed with soil samples. For the 16 spiked individual PAHs, the recoveries were from 70.4% to 117%. The recoveries of deuterated PAHs ranged from 75% to 117%. The method limits of detection (MDL) ranged from 0.01 ng g<sup>-1</sup> to 0.46 ng g<sup>-1</sup>. A method blank (anhydrous sodium sulfate) was coupled with each batch of 12 samples, and the target compounds were under MDLs. All glassware was rinsed with dichloromethane and *n*-hexane and then baked at 450 °C for 4 h.

### **Results And Discussion**

#### Levels and congener pattern of PAHs

The concentrations of 16 individual PAHs, *n*-rings PAHs, 7 carcinogenic PAHs ( $\Sigma_{7-car}$ PAHs) and total 16 PAHs ( $\Sigma_{16}$ PAHs) in soils from Jizhou district and Ninghe district in 2001 and 2018 are summarized in Table S1 and Table S2. For Jizhou district in 2001, the  $\Sigma_{16}$ PAHs concentrations ranged from 241 to 777 ng g<sup>-1</sup>, with a mean value of 447 ng g<sup>-1</sup>. The concentrations of  $\Sigma_{7-car}$ PAHs were in the range of 58.4 to 265 ng g<sup>-1</sup>, making up 38.1% of the  $\Sigma_{16}$ PAHs concentrations. Among, 2- and 5-ring PAHs were the predominated congeners with contributions of 37.0% and 28.6%, respectively, followed by 3- (13.2%), 4- (12.0%), and 6-ring PAHs (9.2%). LMW PAHs contributed about 50% to the total PAHs. Among the detected PAHs, NAP, BbF, BkF, and BaP were the major compounds in soils, comprising 37.0%, 9.3%, 8.9%, and 8.9% of the total PAHs, respectively. In 2018, the concentrations of  $\Sigma_{16}$ PAHs in soils from Jizhou district varied from 113 to 1064 ng g<sup>-1</sup>, with a mean of 711 ng g<sup>-1</sup>. The  $\Sigma_{7-car}$ PAHs comprised 24.5% of the total PAHs, varying from 25.3 to 364 ng g<sup>-1</sup>. The relative composition of PAHs ranked from high to low was as follows: 3-ring (68.7%) > 5-ring (20.8%) > 4-ring (5.7%) > 6-ring (3.6%) > 2-ring (1.3%). The ratio of LMW PAHs increased appreciably from 50% to 70%. ANT and DahA were the dominated compounds, accounting for 59.1% and 16.5% of the total PAHs.

As to Ninghe district in 2001, for  $\Sigma_{16}$ PAHs and  $\Sigma_{7-car}$ PAHs in soils, the concentration ranges were 240 to 2410 ng g<sup>-1</sup> and 94.1 to 749 ng g<sup>-1</sup>, and their mean values were 624 ng g<sup>-1</sup> and 219 ng g<sup>-1</sup>, respectively. The  $\Sigma_{7-car}$ PAHs accounted for 36.1% of the  $\Sigma_{16}$ PAHs. The relative composition of PAHs decreased in the following order: 2-ring (36.7%) > 5-ring (25.1%) > 4-ring (14.4%) > 3-ring (14.0%) > 6-ring (9.7%), and the percentage of LMW PAHs was about 50%. In terms of the individual PAHs, NAP, BbF, PHE, BkF, and BaP were regarded as the predominated compounds, with the contributions of 36.7%, 8.1%, 8.0%, 7.8% and 7.8%, respectively. In 2018, the  $\Sigma_{16}$ PAHs concentrations ranged from 202 to 1964 ng g<sup>-1</sup> (mean 718 ng g<sup>-1</sup>), and the  $\Sigma_{7-car}$ PAHs concentrations were in range of 36.4 to 1496 ng g<sup>-1</sup> and contributed to 28.8% of the total PAHs. 2-, 3-, 4-, 5- and 6-ring PAHs accounted for 2.5%, 62.7%, 5.8%, 25.0% and 4.0%, respectively. The ratio of LMW PAHs increased to 65%. In addition, ANT and DahA were the major compounds, accounting for 47.2% and 15.9% of the total PAHs.

In summary, the temporal changes in concentrations and compositions of 16 PAHs for Jizhou district and Ninghe district between 2001 and 2018 were obvious and similar. Over this period, the concentrations of  $\Sigma_{16}$ PAHs of both districts increased, while the  $\Sigma_{7-car}$ PAHs concentrations decreased or increased slightly. Moreover, the percentage of 2-ring PAHs fell from its peak to its trough, and the percentage of 4-ring PAHs also decreased, but the percentage of 3-ring PAHs increased significantly. The ratio of LMW PAHs increased appreciably. ANT and DahA, instead of NAP, BbF, BkF, and BaP, became the dominated compounds. The concentrations of ANT increased dramatically, while NAP and the HMW PAHs, except for DahA and BaP, decreased substantially. Although PAHs are characterized persistently, their removal from soils attributed to photolysis and chemical degradation, biodegradation and volatilization cannot be neglected (Haritash and Kaushik, 2009). Thus, previous studies found that the concentrations of PAHs decreased substantially after burying in soils for a long time (Cao et al., 2017; Choi, 2014). Moreover, PAHs with different rings present different environmental behaviors in soils (Wild and Jones, 1995). HMW PAHs tend to bury in soils for a longer period of time (Wang et al., 2011), and the degradation rate decreases with increasing molecular weight (Sun et al., 2014). LMW PAHs are more readily to be photodegraded and biodegraded (Jones et al., 1989; Wilcke et al., 2005; Wild and Jones, 1995). Therefore, the increase in  $\Sigma_{16}$ PAHs concentration and LMW PAHs ratio in soils after nearly 20 years indicate continuing discharges of PAHs in both Jizhou district and Ninghe district. Besides, as shown in Fig. S1, in Jizhou district and Ninghe district, the percentages of soil samples contaminated and heavily contaminated by PAHs were notably higher (> 60%) in 2018 than those (< 25%) in 2001. The percentages of heavily contaminated soil samples in Jizhou district and Ninghe district increased from 0% to 14%

In addition, it is worth noting that, from 2001 to 2018, the mean  $\Sigma_{16}$ PAHs concentration in soils from Jizhou district increased by 60 %, while that from Ninghe district only rose by 15 %. The major reason may be the different geographical locations. Ninghe district is adjacent to Tianjin coastal new

region, where there has assembled lots of industrial activities such as coking plants, coal-fired power plants, steel mills, oil exploiting and refinery, and petrochemical in the past few decades. Tianjin coastal new region could be a center of PAH emissions because industrial activities are considered to be the major PAH sources (Manariotis et al., 2011; Wolska et al., 2012; Zhang et al., 2019). Transfer from air to soil is the most important interface process for PAH flux in Tianjin, resulting in very high flux around the industrial area (Tao et al., 2003, 2004). Additionally, more than 90% of the PAHs entering into surface soils attribute to the dry and wet deposition (Wild and Jones, 1995). Therefore, the constant PAH contamination from Tianjin coastal new region may be the main reason for keeping soil PAHs in Ninghe district at a relatively high level. However, Jizhou district is located in the outer suburbs of Tianjin, far away from the areas with severe contamination of PAHs. Many studies in recent years have argued that various and scattered sources, such as industrial facility, traffic, cooking, and space heating in a city, contribute to the regional baseline deposition of PAHs, which is also influenced by the level of economic development and the degree of urbanization and industrialization (Peng et al., 2011, 2013, 2016a; Wang et al., 2015, 2018; Zhang and Chen, 2017). From 2004 to 2016, the number of Jizhou GDP increased by 500%, and the gross product of construction industry in this district increased from 1.5 billion yuan in 2008 to 9.1 billion yuan in 2016. Thus, the relatively larger growth of PAH level in soils from Jizhou district was in part attributed to the local increasingly rapid economic development and urbanization.

Compared with the results reported in worldwide other researches, the concentrations of total PAHs in soils from Jizhou district and Ninghe district in 2018 were at middle level. As shown in Table S3, the  $\Sigma_{16}$ PAHs concentrations were far lower than those in urban and rural soils from Chengdu, China (3110 ng g<sup>-1</sup>) (Zheng et al., 2018), Bergen, Norway (6780 ng g<sup>-1</sup>) (Haugland et al., 2008), and Glasgow, UK (11900 ng g<sup>-1</sup>) (Morillo et al., 2007), and comparable to those in urban soils from Changshu, China (641 ng g<sup>-1</sup>) (Cao et al., 2017) and Torino, Italy (857 ng g<sup>-1</sup>) (Morillo et al., 2007), as well as agricultural soils from Delhi, India (830 ng g<sup>-1</sup>) (Agarwal et al., 2009) and Czech Republic (847 ng g<sup>-1</sup>) (Holoubek et al., 2009). However, they were also substantially higher than those in urban, rural and agricultural soils collected globally, such as Hong Kong (54.6 ng g<sup>-1</sup>) (Zhang et al., 2006), Shanghai (360 ng g<sup>-1</sup>) (Jia et al., 2017) and Xinzhou in China (202 ng g<sup>-1</sup>) (Zhao et al., 2014), Korea (236 ng g<sup>-1</sup>) (Nam et al., 2003), and Poland (252 ng g<sup>-1</sup>) (Maliszewska-Kordybach et al., 2009).

#### Source apportionment using molecular diagnostic ratios

PAH molecular diagnostic ratios are used to qualitatively distinguish emission sources of PAHs in many studies (Chen et al., 2018; Qi et al., 2019; Tobiszewski and Namieśnik, 2012; Wang et al., 2010; Xing et al., 2020; Yunker et al., 2002). Four diagnostic ratios were used to perform PAH source apportionment in this study (Fig. 2). In 2001, for all of samples from Jizhou district, the values of FLA/(PYR + FLA) were greater than 0.5, for 63.2% of samples, ANT/(ANT + PHE) values were greater than 0.1, for 57.9% of samples, IcdP/(IcdP + BghiP) values were greater than 0.5, and for 68.4% of samples, BaA/(BaA + CHR) values were in the range of 0.2-0.35, indicating that coal and biomass combustion is the primary source of PAHs. Besides, 31.6% and 36.8% of samples having BaA/(BaA + CHR) and ANT/(ANT + PHE) ratio less than 0.2 and 0.1 imply that petroleum is, to a certain degree, an important contributed source. As for Ninghe district, the values of FLA/(PYR + FLA) were greater than 0.5 for 100% of samples, IcdP/(IcdP + BghiP) values were greater than 0.5 for 71.4% of samples, and ANT/(ANT + PHE) values were greater than 0.1 for 42.9% of samples, corresponding to the important contribution of coal and biomass combustion to PAH pollutions. High percent of samples having BaA/(BaA + CHR) and ANT/(ANT + PHE) ratios less than 0.2 and 0.1 suggests that petroleum is another emission source which cannot be ignored.

For samples in Jizhou district collected in 2018, 82.1% of FLA/(PYR + FLA) values were greater than 0.5, 100% of ANT/(ANT + PHE) values were greater than 0.1, 78.6% of IcdP/(IcdP + BghiP) values were greater than 0.5, and 53.6% of BaA/(BaA + CHR) values were greater than 0.35, indicating that coal and biomass combustion is a major PAH source. As for Ninghe district, 82.8% of FLA/(PYR + FLA) values were greater than 0.5, 96.6% of ANT/(ANT + PHE) values were greater than 0.1, 75.9% of IcdP/(IcdP + BghiP) values were greater than 0.5, and 50% of BaA/(BaA + CHR) values were greater than 0.35. These results suggest that biomass and coal combustion account for the main source of PAHs.

To sum up, the diagnostic ratios preliminarily reveal a change of the major PAH sources in these two districts during the urbanization and industrialization process from 2001 to 2018. Over this period, PAHs emissions from petrogenic origins decreased, while those from pyrogenic sources increased substantially.

#### Source identification by positive matrix factorization (PMF) analysis

Because of possible significant changes of molecular diagnostic ratios during the migration from sources to receptors due to different physicochemical properties of the paired species (Lang et al., 2008), some uncertainties could not be excluded only based on these ratios (Galarneau, 2008; Katsoyiannis and Breivik, 2014; Zhang et al., 2005). Therefore, USEPA PMF model 5.0 (USEPA, 2014) was introduced to further identify sources of soil PAHs and quantify their contributions in this study.

The quality of the data for each of PAHs used in the model is based on the signal-to-noise ratio and the percentage of samples with concentrations above MDLs (USEPA, 2014). Firstly, the number of soil samples in either Jizhou district or Ninghe district in 2001 was not sufficient for PMF to derive a convincing result. Secondly, with more than 50% of samples in the two districts having concentrations lower than MDLs in 2001, DahA and BghiP were classified as bad species and were excluded from PMF. Finally, soil PAHs in Jizhou district and Ninghe district showed a similar congener pattern in both 2001 and 2018. Hence, a dataset of 33 samples and 14 species and a dataset of 57 samples and 16 species were respectively introduced into the PMF model to identify soil PAH sources in 2001 and 2018. The model was set to run from 3 to 6 factors, and each run was initialized with different starting points. The PAH profiles in factors for 2001 and 2018 are shown in Fig. 3 and Fig. 4, respectively.

In 2001, as shown in Fig. 3, four appropriate factors were identified by the PMF analysis. Factor 1, explaining 32.1% of the total PAHs, was mainly characterized by NAP, ACE and FLO. NAP is a significant fraction of crude oil and petroleum products (Chen et al., 2013; Dahle et al., 2003; Saha et al., 2009). In addition, the dominance of 2- and 3-ring PAHs is related to petrogenic sources (Hu et al., 2013a; Olajire et al., 2005; Wang et al., 2013b). Therefore, factor 1 indicates petroleum sources.

Factor 2 accounted for 22.1% of the total PAHs and was loaded dominantly by IcdP which usually associates with vehicular emissions (Fraser et al., 1997; Harrison et al., 1996; Motelay-Massei et al., 2005), corresponding to traffic sources. Factor 3 was dominated by ANT and responsible for 12.9% of the total PAHs. Given the fact that ANT is a marker of wood combustion source (Harrison et al., 1996), this factor is considered as biomass combustion.

Factor 4 contributed 32.9% of the total PAHs and had high loadings of PHE, FLA, PYR, CHR, and BaA. Coal combustion mainly produces PAHs dominated by 3- and 4-ring congeners (Li et al., 2012; Qu et al., 2020). FLA, PYR, BaA, CHR are typical markers for coal combustion (Duval and Friedlander, 1981; Harrison et al., 1996; Larsen and Baker, 2003; Simcik et al., 1999). Therefore, factor 4 indicates coal combustion.

As shown in Fig. 4, four appropriate factors were also identified in 2018 by the PMF analysis. Factor 1 was responsible for 18.7% of the total PAHs. This factor was predominated by ACY as well as FLA, and moderately weighted by DahA, BghiP and IcdP. ACY and FLA are predominated PAH compounds emitted by grass or wood combustion (Jenkins et al., 1996; Khalili et al., 1995; Ou et al., 2010). DahA, BghiP and IcdP have been identified as typical tracers of vehicular sources (Fraser et al., 1997; Harrison et al., 1996; Larsen and Baker, 2003; Motelay-Massei et al., 2005; Simcik et al., 1999). Thus, factor 1 is considered as petroleum and biomass combustion. The second factor accounted for 10.1% of the total PAHs and was dominated by FLO, PHE and CHR. FLO and PHE are sometimes used as indicators for coke oven sources (Duval and Friedlander, 1981; Simcik et al., 1999). Therefore, factor 2 can be closely related to coke production.

Factor 3, contributing 63.7% of the total PAHs, was loaded predominantly by NAP, ANT, BaP and DahA, and moderately weighted by ACE, FLO, ACY and BghiP. DahA, NAP, FLO, and ANT are the main tracers of diesel engines (Fraser et al., 1997; Khalili et al., 1995; Motelay-Massei et al., 2005), and ACE, ACY, FLO, BaP as well as BghiP are the main tracers of gasoline engines (Harrison et al., 1996; Khalili et al., 1995; Ravindra et al., 2008). Therefore, factor 3 indicates traffic sources.

Factor 4 contributed 7.6% of the total PAHs and had high loadings of PYR, BaA, BbF and BkF. BkF is a typical marker for industrial coal combustion (Brown and Brown, 2012). Moreover, coal combustion mainly produces PAHs dominated by 3- and 4-ring congeners (Li et al., 2012; Qu et al., 2020). Therefore, factor 4 is considered as coal combustion.

The changes for soil PAHs sources in Jizhou district and Ninghe district that happened within the past 20 years were identified according to the results calculated by PMF model. From 2001 to 2018, the contribution of coal combustion had decreased by three quarters. This is inconsistent with that obtained by molecular diagnostic ratios, which actually supports that the latter has some limitations on the source apportionment of PAHs (Galarneau, 2008; Katsoyiannis and Breivik, 2014; Zhang et al., 2005). The substantial reduction in the contribution of coal combustion may be related to the ban of coal burning for heating in winter. Furthermore, coal was the major source in the form of industrial energy in these two districts in the 2000s. However, clean energy sources, such as electricity or natural gas, have been widely expanded in China in recent years. Hence, changes in the energy structure during the industrialization process may be also responsible for this decrease. In contrast, a significant increase in the contribution of traffic sources (from 22.1% to 63.7%) led to much higher concentrations of ANT as well as DahA and their predominance, and a corresponding rise in soil  $\Sigma_{16}$ PAHs concentrations of Jizhou district and Ninghe district in 2018. The dominance of traffic sources was likely attributed to a huge surge in car use resulted from the rapid development and expansion of urbanization as well as the sustained economic growth, such as the burgeoning local vigorous tourism in Jizhou district.

#### Health risk assessment

The incremental lifetime cancer risk (ILCR) model was introduced to assess age- and pathway-specific potential cancer risks of soil PAHs in Jizhou district and Ninghe district. A detailed description of this model is provided in the Supplementary Content. As shown in Table 1 and Table 2, the orders of magnitude of ILCRs<sub>inhalation</sub> for different ages varied in a range of  $10^{-12}$  to  $10^{-10}$ , about  $10^4$  to  $10^5$  times lower than ILCRs<sub>ingestion</sub> and ILCRs<sub>dermal</sub>. Hence, residents in Jizhou district and Ninghe district possibly exposed to soil PAHs via ingestion and dermal contact, while the exposure via inhalation was negligible.

In 2001, for children, adolescents and adults in Jizhou district, ILCRs<sub>ingestion</sub> and ILCRs<sub>dermal</sub> ranged from  $5.91 \times 10^{-8}$  to  $5.19 \times 10^{-7}$  and from  $1.42 \times 10^{-7}$  to  $8.84 \times 10^{-7}$ , while in Ninghe district, ILCRs<sub>ingestion</sub> and ILCRs<sub>dermal</sub> for these three age groups were from  $6.64 \times 10^{-8}$  to  $1.15 \times 10^{-6}$  and from  $1.59 \times 10^{-7}$  to  $1.95 \times 10^{-6}$ , except one sample with ILCR values greater than  $10^{-6}$ . ILCRs<sub>ingestion</sub> and ILCRs<sub>dermal</sub> in Ninghe district were slightly higher than those in Jizhou district. Totally, the vast majority of samples in these two districts had ILCRs lower than the safe value of  $1 \times 10^{-6}$ , indicating health risks are generally at a safe level.

In 2018, the ILCRs of all exposure pathways for residents were relatively higher than those in 2001. For residents in Jizhou district, ILCRs<sub>ingestion</sub> and ILCRs<sub>dermal</sub> ranged from  $5.90 \times 10^{-8}$  to  $1.72 \times 10^{-6}$  and from  $1.41 \times 10^{-7}$  to  $2.92 \times 10^{-6}$ , respectively. At 11 of the 28 samples, ILCRs<sub>dermal</sub> were higher than  $10^{-6}$  for children, adolescents and adults, and ILCRs<sub>ingestion</sub> were greater than  $10^{-6}$  for children and adults. For Ninghe district, ILCRs<sub>ingestion</sub> and ILCRs<sub>dermal</sub> were from  $7.54 \times 10^{-8}$  to  $1.18 \times 10^{-6}$  and from  $1.80 \times 10^{-7}$  to  $2.01 \times 10^{-6}$ , respectively. For children and adolescents, ILCRs<sub>dermal</sub> were higher

than  $10^{-6}$  at 6 of the 29 samples, but for adults, ILCRs<sub>dermal</sub> were higher than  $10^{-6}$  at 13 samples. It should be noted that there was only one sample with ILCRs<sub>ingestion</sub> greater than  $10^{-6}$  for children and adults. These results indicate higher cancer risks to residents in these two districts in 2018, with dermal contact as the chief exposure pathway. The increase in cancer risks from 2001 to 2018 occurred mainly because the alterations of PAH sources led to the predominance of DahA which has a highest TEF and therefore a strong carcinogenic potency equal to BaP. In view of the fact that DahA is considered as an indicator for the vehicular emission (Fraser et al., 1997; Motelay-Massei et al., 2005), a substitution of diesel and gasoline by clean energies in vehicles and an option of public transit over private cars should be advocated to reduce the health risks to local residents.

# Conclusions

Comparisons of soil PAHs in Jizhou district and Ninghe district between 2001 and 2018 indicate that urbanization can, to a large extent, change sources, pollution levels and congener patterns of these compounds. During the past decades, the total concentrations of soil PAHs in these two rural areas increased due to the rapid urbanization, with the contributions of both 2- and 4-ring PAHs decreased substantially while 3-ring PAHs increased significantly. Instead of NAP, BbF, BkF and BaP, homologues of ANT and DahA became dominated components. Calculated data from the PMF model show that the contribution of traffic sources has nearly tripled, while coal combustion has decreased by three quarters over the past 20 years. Most importantly, predominated PAH emissions changed from coal combustion and petroleum sources to traffic sources may incur a possible substantial increase in cancer risks to the residents.

# Declarations

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### Declaration of interests

I The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

IThe authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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### Tables

Table 1 Age-specific potential cancer risk via exposure to soil PAHs in 2001										
District		Childhood			Adolescence			Adulthood		
		ILCR ingestion	ILCR <sub>dermal</sub>	ILCR inhalation	ILCR ingestion	ILCR <sub>dermal</sub>	ILCR inhalation	ILCR ingestion	ILCR <sub>dermal</sub>	ILCR inhalation
Jizhou	Mean	2.84 × 10 <sup>-7</sup>	3.54 × 10 <sup>-7</sup>	6.01 × 10 <sup>−</sup> 12	1.48 × 10 <sup>-7</sup>	3.69 × 10 <sup>-7</sup>	1.02 × 10 <sup>-</sup> 11	2.72 × 10 <sup>-7</sup>	4.84 × 10 <sup>-7</sup>	1.85 × 10⁻ 11
	Min.	1.14 × 10 <sup>-7</sup>	1.42 × 10 <sup>-7</sup>	2.40 × 10 <sup>−</sup> 12	5.91 × 10 <sup>-8</sup>	1.47 × 10 <sup>-7</sup>	4.06 × 10 <sup>−</sup> 12	1.09 × 10 <sup>-7</sup>	1.93 × 10 <sup>-7</sup>	7.38 × 10⁻ 12
	Max.	5.19 × 10 <sup>-7</sup>	6.47 × 10 <sup>-7</sup>	1.10 × 10 <sup>-</sup> 11	2.71 × 10 <sup>-7</sup>	6.75 × 10 <sup>-7</sup>	1.86 × 10⁻ 11	4.98 × 10 <sup>-7</sup>	8.84 × 10 <sup>-7</sup>	3.38 × 10⁻ 11
Ninghe	Mean	3.59 × 10 <sup>-7</sup>	4.47 × 10 <sup>-7</sup>	7.58 × 10⁻ 12	1.87 × 10 <sup>-7</sup>	4.66 × 10 <sup>-7</sup>	1.28 × 10 <sup>-</sup> 11	3.44 × 10 <sup>-7</sup>	6.11 × 10 <sup>-7</sup>	2.33 × 10⁻ 11
	Min.	1.27 × 10 <sup>-7</sup>	1.59 × 10 <sup>-7</sup>	2.69 × 10 <sup>−</sup> 12	6.64 × 10 <sup>-8</sup>	1.66 × 10 <sup>-7</sup>	4.56 × 10 <sup>−</sup> 12	1.22 × 10 <sup>-7</sup>	2.17 × 10 <sup>-7</sup>	8.29 × 10 <sup>−</sup> 12
	Max.	1.15 × 10 <sup>-6</sup>	1.43 × 10 <sup>-6</sup>	2.42 × 10 <sup>-</sup> 11	5.97 × 10 <sup>-7</sup>	1.49 × 10 <sup>-6</sup>	4.10 × 10 <sup>−</sup> 11	1.10 × 10 <sup>-6</sup>	1.95 × 10 <sup>-6</sup>	7.45 × 10⁻ 11

Table 2 Age-specific potential cancer risk via exposure to soil PAHs in 2018

District		Childhood			Adolescence			Adulthood		
		ILCR ingestion	ILCR <sub>dermal</sub>	ILCR inhalation	ILCR ingestion	ILCR <sub>dermal</sub>	ILCR inhalation	ILCR ingestion	ILCR <sub>dermal</sub>	ILCR inhalation
Jizhou	Mean	7.38 × 10 <sup>-7</sup>	9.20 × 10 <sup>-7</sup>	1.56 × 10⁻ 11	3.84 × 10 <sup>-7</sup>	9.58 × 10 <sup>-7</sup>	2.64 × 10 <sup>-</sup> 11	7.07 × 10 <sup>-7</sup>	1.26 × 10 <sup>-6</sup>	4.80 × 10 <sup>-</sup> 11
	Min.	1.13 × 10 <sup>-7</sup>	1.41 × 10 <sup>-7</sup>	2.40 × 10 <sup>−</sup> 12	5.90 × 10 <sup>-8</sup>	1.47 × 10 <sup>-7</sup>	4.05 × 10 <sup>−</sup> 12	1.09 × 10 <sup>-7</sup>	1.93 × 10 <sup>-7</sup>	7.37 × 10 <sup>−</sup> 12
	Max.	1.72 × 10 <sup>-6</sup>	2.14 × 10 <sup>-6</sup>	3.63 × 10⁻ 11	8.95 × 10 <sup>-7</sup>	2.23 × 10 <sup>-6</sup>	6.14 × 10 <sup>−</sup> 11	1.65 × 10 <sup>-6</sup>	2.92 × 10 <sup>-6</sup>	1.12 × 10 <sup>-</sup> 10
Ninghe	Mean	5.23 × 10 <sup>-7</sup>	6.52 × 10 <sup>-7</sup>	1.11 × 10⁻ 11	2.72 × 10 <sup>-7</sup>	6.79 × 10 <sup>-7</sup>	1.87 × 10⁻ <sup>11</sup>	5.01 × 10 <sup>-7</sup>	8.90 × 10 <sup>-7</sup>	3.40 × 10⁻ 11
	Min.	1.45 × 10 <sup>-7</sup>	1.80 × 10 <sup>-7</sup>	3.06 × 10 <sup>−</sup> 12	7.54 × 10 <sup>-8</sup>	1.88 × 10 <sup>-7</sup>	5.17 × 10 <sup>−</sup> 12	1.39 × 10 <sup>-7</sup>	2.46 × 10 <sup>-7</sup>	9.40 × 10 <sup>−</sup> 12
	Max.	1.18 × 10 <sup>-6</sup>	1.47 × 10 <sup>-6</sup>	2.50 × 10 <sup>-</sup> 11	6.15 × 10 <sup>-7</sup>	1.53 × 10 <sup>-6</sup>	4.22 × 10 <sup>-</sup> 11	1.13 × 10 <sup>-6</sup>	2.01 × 10 <sup>-6</sup>	7.68 × 10⁻ 11

## **Figures**



#### Figure 1

Map of the study area and the sampling site in 2018 (a), and 2001 (b) (modified from a study that published by Wang et al. (2003)). Industrial areas are marked in cyan. Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.



#### Figure 2

Plots of PAH molecular diagnostic ratios in 2001 (left) and 2018 (right)



#### Figure 3

Source profiles of each factor in 2001 obtained from PMF model







### Figure 4

Source profiles of each factor in 2018 obtained from PMF model

## **Supplementary Files**

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