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New observations on PAH pollution in old heavy industry cities in northeastern China

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This study investigated the distinctive PAHs adsorbed on street dust near various industries in the three typical industrialized cities of Daqing (DQ), Harbin (HEB) and Jilin (JL) in northeastern China. The mean ∑PAHs concentrations in street dust of DQ, HEB and JL were 1.84, 4.87, 12.38 μg/g, respectively. Typical petroleum resource city DQ had higher proportions of low and medium ringed PAHs with higher proportions of phenanthrene (Phe), naphthalene (Nap), fluoranthene (Flua) and chrysene (Chr) at industrial sites. Typical chemical processing city JL had higher proportions of medium and high ringed PAHs with higher proportions of Flua, benz[a]anthracene (BaA), pyrene (Pyr) and benzo[a]pyrene (BaP) at industrial sites. Phe, Flua, Pyr and Chr were four major PAHs from most studied industries. The distinctive PAH emissions from the ferroalloy plant were BaA and BaP. BaA and BaP concentrations decreased by 90% at sites more than 2 km away from the ferroalloy plant.

1. Introduction

Similar to many countries in the world, the heavy industries in China were built in relatively concentrated areas for efficiency during the fast industrialization period in the 1950s and 1960s. The northeastern area of China, including Heilongjiang, Jilin and Liaoning provinces, was the old heavy industrial base. This area is rich in coal, iron ore and oil resources for these industries (Kong et al., 2011). Similar to the northeastern area of the United States, this area has many industrialized cities which are concentrated with industries such as the iron and steel industry, machinery manufacturing, automobile manufacturing, oil processing, etc. (Kong et al., 2011; Sun et al., 2014) These industries were established to support economic development, especially at the beginning of the country's developing period. Although having contributed to the most basic and important products throughout their peak time, these industries have emitted millions of tons of pollutants into the surrounding environment (Guo et al., 2007; Kong et al., 2011; Sun et al., 2014), which are hard to control and continuously threaten the health of people.

Heavy industries usually involve incomplete combustion and pyrogenic processes of organic materials, such as the fuel combustion of coal, oil, gas, wood, etc. (Khalili et al., 1995; Gateuille et al., 2014; Hong et al., 2015). These processes usually emit considerable amounts of persistent volatile organic pollutants (POPs); among them, polycyclic aromatic hydrocarbons (PAHs) have drawn much attention due to their wide existence, complexity in forms and transformations, and, most importantly, serious toxicity to the ecosystem (Saeedi et al., 2012; Lin et al., 2015). For example, the PAH concentrations in the fly ash in the four processes of an iron and steel facility were as follows: cold forming (6.2 mg/g) > coke making (1.8 mg/g) > hot forming (1.6 mg/g) > sintering (0.5 mg/g) (Tsai et al., 2007). The sintering process exists in many industries, such as the coking process in coking plants, steel and iron industries. It mainly produces PAHs via unsealed oven doors and the processes of charging, pushing and cooling (Mastral and Callen, 2000). The major PAH species in the sintering process are acenaphthylene (Acpy), phenanthrene (Phe), benzo[k]fluoranthene (BkF) and benzo[a]pyrene (BaP) (Tsai et al., 2007). The predominant PAHs in the coke oven emissions are naphthalene (Nap), Acpy, Phe, fluorine (Flu), anthracene (Ant) and fluoranthene (Flua) (Khalili et al., 1995). Booth and Gribben (2005) showed that the three types of aluminum production methods (Soderberg smelter, prebake smelter, and anode/paste plant) demonstrated similar PAH emissions; Phe, Flua, and pyrene (Pyr) were the three most abundant PAHs, accounting for 54–69% of the total 15 PAHs measured.

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In addition to industrial processes, PAHs are also generated by other anthropogenic activities such as vehicular emissions, residential heating, etc. (Adetona et al., 2013; Gunawardena et al., 2014). Compared to the other sources during weekdays, vehicular sources are predominant in gas phase PAHs (Gunawardena et al., 2012). Gunawardena et al. (2014) found that gasoline powered vehicles was the main cause for PAH accumulation on road surfaces.

As one of the most important environment indicators, street dust is the sink of urban pollutant emissions and also works as the major source of pollution in runoff (Lau and Stenstrom, 2005; Tuyen et al., 2014). This study focused on the distinct contribution of various industries on the PAHs in street dust of heavy industrial cities in northeastern China. The primary objectives included (1) determining the distinct PAHs in the street dust near different types of heavy industries, (2) investigating the influences of different industrial processes, distance, and land-use distributions on PAH distributions, and (3) identifying the major sources of PAHs.

2. Materials and methods

2.1. Sampling city description

Three typical heavy industrial cities of Daqing (DQ), Harbin (HEB), and Jilin (JL) from the northeastern heavy industry base were selected as the study sites. The study cities have a temperate semi-humid continental monsoon climate with the average temperature between −18.5 and 24.8 °C. DQ City is a typical oil city with the largest oilfield in China, leading in the petrochemical industry with crude oil processing industry chains (NBSC, 2013a). HEB City is the traditional third biggest heavy industrial city in China. The main industries in HEB include food, equipment manufacturing, petrochemical and pharmaceutical industries (NBSC, 2013a). JL City is an important chemical industry base in China, which is dominated by the chemical, metallurgy, electric power and automobile industries (NBSC, 2013a). Overall, there were 413, 1148, and 1121 up-scale industrial enterprises with a prime operating revenue of more than 20 million RMB Yuan (Chinese currency, the average exchange rate in 2014 was 1 RMB = 0.1628 USD) per year in DQ, HEB, and JL, respectively, in 2012 (NBSC, 2013b). Among them, approximately 64.65%, 54.53% and 64.59% were heavy industries (NBSC, 2013b). More information about the study cities are shown in Table 1:

2.2. Different PAH emissions from industries in DQ, HEB, and JL

Table S1 provides detailed information on the top 20 prime operating revenue companies located in the centers of DQ, HEB, and JL. The major PAH emission processes are also illustrated. The multiple oil mining spots of Daqing Oilfield Co., Ltd (DQ-i1) and PetroChina Daqing Petrochemical Company (DQ-i2) are the two biggest heavy industrial plants, accounting for 80% of the energy production in the DQ central city area (NBSC, 2013a). PAH emissions from the oil and gas mining industry are mainly from oil spilling and volatile oil gases. HEB city is largely involved with petrochemical products and metal processing industries. PetroChina Harbin Petrochemical Company (HEB-i1) and Harbin Boiler Company Limited (HEB-i2) are the two largest heavy industrial plants in the Harbin central area. PAHs are emitted from crude oil refining, producing, welding, metal smelting and coal combustion in the boilers. Jilin City is mainly involved with chemical processing industries. PetroChina Jilin Petrochemical Company (JL-i1) and Jilin Chemical Group Company (JL-i2) are the two largest heavy industrial plants in the JL central area. PAH emissions are mainly from crude oil refining and the coal-fired boiler.

2.3. Sampling site description and sample collection

A total of 21/0, 21/2 and 23/4 street dust/surface soil samples were approximately evenly collected in the centers of HEB, JL and DQ on October 12, 2011, October 19 and October 21, 2012, respectively. Sampling sites within a city were represented with absolute numbers of 1, 2, 3, etc. in Fig. 1 (Samples of HEB3 and JL6 were lost). The borders of the sampling region in Fig. 1 were determined by expanding 3 km beyond the furthest sampling sites. The PAH emission related heavy industries in each city were marked with i1, i2, i3, etc. in Fig. 1. Due to the large amount of up-scale heavy industry companies in each city, only the top 20 prime operating revenue companies within the plotted area in each city were shown in Fig. 1. DQ-i1 in DQ city were marked with codes i1a, i1b, and i1c. More information on the coded industries can be found in Table S1. The sampling sites belonged to five functional areas, including industrial, commercial, residential, street and park.

Sampling was conducted at least seven days after a rainfall event. Street dust samples (300–500 g each site) were collected within 0.5 m from the curbstones or street edges using a small clean brush. The dust samples were air-dried for at least 15 days and then sieved through a screen with 500 μm openings to remove large sands, stones, plant debris, etc. The top 15 cm surface soil samples were collected with a metal shovel and well mixed. After air dried for at least three weeks, the soil samples were also sieved through a 500 μm screen to remove large stones, plant debris, etc. Then the seived soil samples were grounded into particles less than 200 μm for further chemical analysis.

2.4. Chemical reagents and PAH extraction and analysis

Three standard solutions were purchased from J&K chemical Ltd., USA: (1) a mixed standard solution of 16 PAHs (AccuStandard, Inc. USA) including Nap, Acpy, acenaphthene (Ace), Flu, Phe, Ant, Flua, Pyr, benz[a]anthracene (BaA), chrysene (Chr), BkF, benzo[b]fluoranthene (BbF), BaP, indeno[1,2,3-cd]pyrene (IND), dibenz[a, h]anthracene (DbA), and benzo[g,h,i]perylene (BghiP); (2) a mixed deuterated PAH standard solution for recovery efficiency measurement containing naphthalene-d8, acenaphthene-d10,

Table 1
Geological and economic information of DQ, HEB and JL.

City name	Total/central city area (km^2)	Population (10^6 inhab.)	2nd industry's GDP[a] (10^9 Yuan)	2nd industry's GDP proportion[b] (%)	Energy consumption[c] (10^6 ton standard coal/year)		
					Raw coal	Crude oil	Gasoline diesel
DQ[d]	22,161/5107	2.9	323.64	80.9	7.40	19.83	0.44
HEB[e]	53,068/7086	10.6	163.89	36.1	13.27	5.03	0.10
JL[f]	27,120/3636	4.4	120.75	49.7	8.14	11.96	0.39

[d, e, f] data from NBSC, 2013a.
[a] Gross domestic product.
[b] The proportion of the 2nd industry's GDP to the sum of first, second, and third industries in 2012.
[c] For the up-scale industrial companies in 2012.