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# Emission characteristics and size distribution of polycyclic aromatic hydrocarbons from coke production in China

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ABSTRACT

Coking is regarded as a major source of atmospheric polycyclic aromatic hydrocarbons (PAHs), but few researches have been conducted on the emission characteristics of PAHs from coke production. In this study, emissions of size-segregated particulate matter (PM) and particle-bound PAHs emitted from charging of coal (CC) and pushing of coke (PC) in four typical coke plants were determined. The emission factors on average, sums of CC and PC, were 4.65 mg/kg, 5.96 mg/kg, 19.18 μg/kg and 20.69 μg/kg of coal charged for $PM_{2.1}$ (≤ 2.1 μm), PM, PAHs in $PM_{2.1}$ and total-PAHs, respectively. PM and PAHs emission from plants using stamp charging were significantly more than those using top charging. The profile of PAHs in PM with size ≤ 1.4 μm ($PM_{1.4}$) emitted from CC process were similar with that from PC, however, it revealed obviously different tendency for PAHs in PM with size > 1.4 μm, indicating the different formation mechanism for coarse particles emitted from CC and PC. Size distributions of PM and PAHs indicated that they were primarily connected with $PM_{1.4}$, and the contributions of $PM_{1.4}$ to PM and PAHs emitted from the plants using stamp charging were higher than those using top charging. Some improved technology in air-pollution control devices should be considered in coke production in future based on the considerable impacts of $PM_{1.4}$ and PAHs on human health and ambient air quality.

## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous harmful organic compounds generated by incomplete combustion happened to organic materials, such as coal, gasoline, and diesel fuel. It was estimated that the total emission of PAHs was 520 Gg $year^{-1}$ in 2004 and China was the largest emitting country with 114 Gg $year^{-1}$ (Zhang and Tao, 2009). Chinese energy consumption increases continuously along with fast growth in its population and economy. Thus, the total emissions of PAHs have been on constant rise for several decades.

It has been well known that PAHs are strong mutagens and potential human carcinogens. They are often associated with smaller particles so that they can enter into deeper part of the lung, which means that they are more harmful to people's health (Duan et al., 2005; Maté et al., 2010; Tan et al., 2016). Thus, it is of great importance to analyze particle size distribution of PAHs when assessing their possible influence on human health. Besides, characterization on the size distribution of PAHs emitted from various sources can provide chemical and physical information in understanding their formation processes, assessing their possible mobility after emission and offering proper management methods. According to available information, several researches on PAHs size distributions have focused on generators emission (Tsai et al., 2015), wood and biomass combustion (Hays et al., 2003; Keshtkar and Ashbaugh, 2007; Shen et al., 2011a; Shen et al., 2013; Venkataraman et al., 2002; Yang et al., 2006b), coal combustions (Chen et al., 2004; Shen et al., 2010) and vehicle emissions (Eiguren-Fernandez and Miguel, 2012; Lu et al., 2012; Riddle et al., 2007a,b; Zielinska et al., 2004). Although industrial process accounted for a considerable share (> 16%) of PAH emission in China (Xu et al., 2006), it has been relatively less studied (Arditsoglou et al., 2004).

It is well known that China is the biggest coke-producing country around the world, and annual coke output in China is over 250 million tons (NBSC, 2012). During coking, secondary reactions happen when the coal is heated in an atmosphere without oxygen. It has been proved that aromatization reaction, one of the secondary reactions, is a major way for the formation of PAHs (Kozielska and Konieczyński, 2015; Mastral and Callén, 2000; Mu et al., 2013; Mu et al., 2014). In major Chinese cities whose populations are over one million, PAHs emitted from coking accounts for 49% of the total PAHs emission (Zhang et al., 2007). Epidemiological studies have also implicated that coke oven

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**Table 1**
Basic information of the investigated coke plants.

| Denotation | Plant A | Plant B | Plant C | Plant D |
|---|---|---|---|---|
| Annual capacity (thousand tonne) | 556 | 936 | 252 | 864 |
| Technique of coal charging | TC[a] | TC | SC[b] | SC |
| Height of ovens (m) | 4.30 | 6.00 | 3.20 | 4.30 |
| Air pollution control device (APCD) | BF[c] | BF | BF | BF |
| Total average exhaust velocity (m/s) | 13.50[d] 32.22[e] | 11.05[d] 15.04[e] | 31.01[d] 33.11[e] | 36.31[e] |
| Combustion temperature of gas in the battery flues (°C) | 248 | 295 | 239 | 276 |
| Coking temperature (°C) | 1335 | 1270 | 1380 | 1375 |
| Coking time (h) | 25 | 23 | 24 | 36 |
| Output rate (T/d) | 1524.4 | 2564 | 690 | 2376 |

[a] Top charging.
[b] Stamp charging.
[c] Baghouse filter.
[d] Termed as exhaust gas emitted during charging of coal.
[e] Termed as exhaust gas emitted during pushing of coke.

workers are at higher risk of lung cancer, and PAHs is identified as a major contributor to carcinogenic risk among all the coke oven emissions (Duan et al., 2005; IARC, 1987). Several researches have been conducted on PAH emission levels from fugitive emission of coke oven battery in Poland (Kozielska and Konieczyński, 2015), the process of coke making in Taiwan (Tsai et al., 2007), and the flue gases of coke production in U.S. (EPA, 2012). Our research group has also examined the emission characteristics of PAHs in both particulate and gaseous phase as well as heavy metals from specific mechanical processes and fugitive emissions in Chinese coke production (Liu et al., 2014; Mu et al., 2013; Mu et al., 2012; Mu et al., 2014). However, investigation on the size distribution concerning particle-bound PAHs pertaining to specific mechanical processes in coking is not found because it is difficult to take samples and the coke production process is of great complexities.

The aims of the study were to acquire emission characteristics of particulate phase PAHs and to find out size distribution of PAHs emitted from charging of coal (CC) and pushing of coke (PC). The information acquired will be helpful to understand the influence of PAHs caused by coking on both regional and global air quality, and also on human health.

## 2. Experimental methods

### 2.1. Sampling

Shanxi is the biggest province in terms of coke production in China, accounting for about 40% of Chinese coke production and 60% of Chinese coke export (Yang et al., 2006a). Four coke plants using different techniques and having different production capacities in Shanxi were selected to be studied. Their basic information is given in Table 1. The Height of coke ovens included 3.2 m, 4.3 m and 6.0 m, and the annual capacity of coke in these plants ranged from $252 \times 10^3$ to $936 \times 10^3$ ton year$^{-1}$ with an average of $652 \times 10^3$ ton year$^{-1}$. There are some differences in coke oven volumes of the four plants, the charging technique in plant A and B is also different from that in plant C and D, with A and B adopting top charging compared with stamp charging for C and D. Furthermore, bag filter (BF) was applied in all these tested plants to remove particulate matter (PM) from the flue gases.

During the process of coking, coal was loaded into coke ovens and heated at high temperatures (900–1100 °C) in the absence of oxygen until most volatile components in it are volatilized. The operation of each oven was cyclic, and the individual oven was loaded and emptied at similar time intervals within the cycle. When charging coal into the ovens, the gases generated were sucked into the duct and then were cleaned by passing through the BF, and finally emitted into the air through the stack (used for the emissions from CC). When it came to the last part of the cycle, doors on both sides of coke oven were removed, and the coke was unloaded by a big ram which was linked to a pusher machine. By means of a coke guide, the coke was finally unloaded into a railroad car called a quench car. Pushing emissions was collected by traveling hoods and transported to the BF by fixed duct, and finally the gas after dedusting emitted into the air through the stack (used for the emissions from PC). At last, quench car transported the coke to quench towers where the coke was cooled down by water in order to avoid coke burning when it is exposed to air. Detailed production operation in the four plants is available in our previous publications (Mu et al., 2013; Mu et al., 2012; Mu et al., 2014). In the present study, samples from flue gas for CC and PC during coking processes were collected to investigate the characterization and size distribution of PAHs in particles. For a few coke plants in China, such as Plant D, special techniques are used for CC, and hardly any exhaust gas is released. Therefore, no stack was built for conducting the gas released when the coal is charged into the ovens.

The sampling system and procedure were elaborated elsewhere (Mu et al., 2013) and were shortly summarized here. Isokinetic sampling system was used to collected fly ash samples. The system, which has been used in our previous study, has a device for cooling, a probe for sampling, and a sampler (Mu et al., 2013). Stainless steel is used in the production of all parts of the system, and all gaskets were made of Teflon so that organic contamination could be prevented. Before taking samples, the whole sampling system were cleaned and examined for air tightness. According to the shape of cross-section and size of the stacks in these selected coke plants, one sampling point in each stack was determined. On the basis of the operating conditions of PC and CC, a sampling period lasting 2 to 5 min was needed for each run, and each sample includes three runs or more. Flue gas conditions, including smoke temperature, relative humidity, and velocity of flue gas were recorded during sampling. Residual in the pipes and loss of emission had not been observed. In addition, the samples were not diluted with clean gas before collected in the study because the dilution might influence nucleation and particle size distribution of compounds to be studied (Lipsky and Robinson, 2006; Roden and Bond, 2006). The same sampling strategy has been used in many studies for conducting PAHs sampling on different emission sources (Lee et al., 2004; Shen et al., 2011b; Shen et al., 2012).

The sampler used in this study was a high-volume cascade impactor with a flow rate of 0.565 m$^3$/min (staplex 234, Staplex® Company), and it can segregate particles into five categories with different diameters of

**Table 2**
Emission factors of particulates and PAHs from coke over charging and pushing (mg/kg coal for particulates, μg/kg coal for PAHs, $n = 3$).

| Compound | Plant A | | Plant B | | Plant C | | Plant D |
|---|---|---|---|---|---|---|---|
| | CC | PC | CC | PC | CC | PC | PC |
| $PM_{2.1}$ | 1.22 ± 0.67 | 0.75 ± 0.52 | 0.42 ± 0.08 | 0.73 ± 0.07 | 4.18 ± 3.07 | 5.89 ± 4.14 | 3.47 ± 1.07 |
| PM | 1.63 ± 0.19 | 0.98 ± 0.30 | 0.62 ± 0.21 | 1.12 ± 0.32 | 5.56 ± 0.56 | 7.55 ± 1.13 | 3.77 ± 0.40 |
| PAHs in $PM_{2.1}$ | 0.50 ± 0.11 | 0.29 ± 0.09 | 0.23 ± 0.10 | 0.46 ± 0.14 | 44.41 ± 27.23 | 11.69 ± 7.04 | 4.08 ± 2.98 |
| Total PAHs | 0.60 ± 0.04 | 0.34 ± 0.01 | 0.26 ± 0.08 | 0.59 ± 0.21 | 47.56 ± 32.95 | 12.78 ± 8.03 | 4.49 ± 3.34 |