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Coke workers' exposure to volatile organic compounds in northern China: a case study in Shanxi Province

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Abstract China is the largest coke producer and exporter in the world, and it has been a major concern that large populations of coke workers are exposed to the associated air pollutants such as volatile organic compounds (VOCs). This study aimed to preliminarily quantify the potential exposure to VOCs emitted from two representative coking plants and assess the potential health risks. Air samples from various stages of coking were collected from the topside of coke ovens and various plant areas and then analyzed for benzene, toluene, ethylbenzene, and xylene (BTEX). The time-weighted average (TWA) concentrations were used to quantify the coke oven emission (COE). The TWA concentrations for benzene were 705.6 and 290.4 μg m^{-3} in plant A and plant B, respectively, which showed a higher exposure level than those reported in other countries. COE varied on the topside of coke ovens during charging and pushing processes, from 268.3 to 1197.7 μg m^{-3} in plant A and 85.4–489.7 μg m^{-3} in plant B. Our results indicate that benzene exposure from the diffusion of tar distillation also exerts significant health risks and thus should also be concerned. Charging and pushing activities accounted for nearly 70 % of benzene dose at the topside, and the benzene exposure risks to the coke oven workers in China were higher than those reported by US EPA. Compared to the reported emission sources, the weight-based ratios of average benzene to toluene, ethylbenzene, and xylene in different COE air samples showed unique characteristic profiles. Based on the B/T ratios from this work and from literatures on several major cities in northern China, it was evident that COE contributes significantly to the severe pollution of VOCs in the air of northern China. Future more rigorous studies are warranted to characterize VOC emission profiles in the stack gas of the coking processes in China.

Keywords Coke workers · Volatile organic compounds · Benzene · Risk assessment · Environmental implication

Introduction

Concern about coke workers' exposure to coke oven emissions (COEs) has been growing over the last several decades. During a coking cycle, a substantial amount of chemicals known as COE can be emitted from activities of charging the coking coal and pushing the hot coke and by leaking through numerous cracks in the oven door and topside ports. Primarily, chemical compounds in COE include polycyclic aromatic hydrocarbons (PAHs), e.g., benzo(a)pyrene (BaP) as well as volatile organic

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compounds (VOCs), e.g., benzene (Kirk-Othmer 1979; Eisenhut et al. 1990). There has been considerable epidemiological evidence suggesting that COEs have been carcinogenic to workers (IARC 1984, 1987).

Many studies have indicated that coke workers are often exposed to high levels of carcinogenic PAHs and VOCs, such as BaP and benzene (e.g., Kivistő et al. 1997; Binková et al. 1998; Grazyna et al. 2004). These studies also revealed that coke workers' exposure to COE is significantly influenced by job locations and can vary in the coking process. It is generally observed that coke workers are exposed to highest COE on the topside of coke oven and during tar distillation station (Bieniek 1998; Strunk et al. 2002; Hu et al. 2006; Yang et al. 2007). Moreover, the exposure can also vary even on top of coke oven. For instances, the Larry car operators, lidmen, and door machine operators stationed very close to the oven are more vulnerable to the toxic volatiles released from the topside and the sides during charging and/or coke pushing, when the highest mean breathing zone concentrations are typically observed (Keimig et al. 1986; Chen et al. 1999). COE is not only hazardous to coke oven workers, but also dispersible to the surrounding atmosphere. It had been reported that high concentrations of COE (benzo(a)pyrene and benzene) decreased significantly following the coke oven closure (Parodi et al. 2005; Federico et al. 2005).

China is the largest coke producer in the world with a coke output exceeding 250 million tons per year (NBSC 2012). As the coke output continues to soar, the environmental challenge becomes increasingly serious. Although the coking technologies in China have been improved greatly driven by the associate profits as well as the relevant environmental policies (Li 2000; Yang et al. 2006; Chen and Polenske 2006), Chinese coke workers still remain exposed to high levels of COE (Wang et al. 2003; He et al. 2005; Qian et al. 2006). And also, the heavy coke production in the northern China at least partially contributes to the high levels of particulate matter and other pollutants in the atmosphere of this region (Barletta et al. 2005; Duan et al. 2008; MEP 2005–2014). However, there are few data available on exposure of VOCs to Chinese coke workers and implications to the environment at large, especially after the enacting of the Admittance Conditions of Coking Industry prescribed by the Chinese National Development and Reform Commission (CNDRC) in 2004 (CNDRC 2004).

The overall goal of this study was to evaluate the exposure and associated health impacts of VOCs emitted from various coking processes. The specific objectives were to (1) collect and analyze air samples from various coking activities at the topside of coke oven and plant areas; (2) assess the health risks associated with benzene (B), toluene (T), ethylbenzene (E), and xylene (X); and (3) evaluate the overall environmental effect of coke production on the air quality in northern China.

Sampling and analysis

Sampling design

As described by US EPA, coke is produced by pyrolysis of coking coal at 900–1300 °C in narrow, rectangular refractory brick ovens arranged in groups of ≤100 ovens (US EPA 2001). Figure 1 presents the distribution of coke production and coke plants in China (Fig. 1a), schematic layout of a typical coke plant (Fig. 1b), and makeup of coke oven (Fig. 1c), which also applies to the experimental plants. Shanxi Province is the largest province for coke production in China, accounting for 40 % of total coke production and 60 % of coke export in China (Li 2000; Chen and Polenske 2006). Air sampling was conducted in two representative coking plants (A and B) in Shanxi Province, where coking has been heavily practiced for decades. The basic information of the two coke plants is described in Table 1. Except for the different oven volume, the coal charging technique in plant B was stamp charging compared with top charging in plant A, which largely decreased COE into the atmosphere. The waste gas from charging and pushing was directly discharged in plant A, and this type of coke ovens (height=2.8 m) has been very rare in China. The plant B was erected with a central dust catcher and desulfurizer station, which was considered to meet the Chinese national production requirements by CNDRC and the environmental regulations of Ministry of Environmental Protection (MEP) of People's Republic of China.

Sampling was carried out during August 10–20, when the weather conditions were 23–30 °C for air temperature, no wind, or wind speed ≤3 m/s. The sampling locations include the topside of coke oven and plant areas as shown in Fig. 1. The coking plants were operated 24 h a day and 7 days a week. The topside samples were collected by simulating the potential

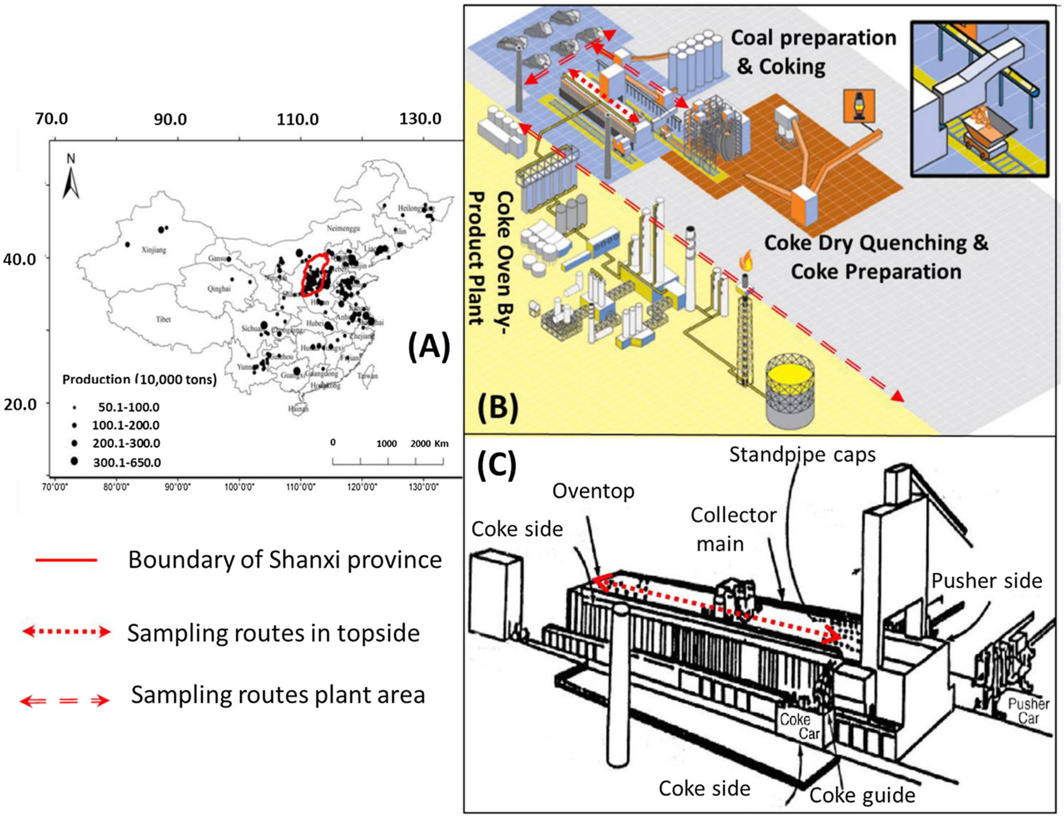

Fig. 1 The distribution of coke production and coke plants in China (**a**), schematic layout of a typical coke plant (**b**), and makeup of coke oven (**c**) and sampling routes in the topside of coke oven and plant area

exposures of coke oven workers during their routine work activities. For example, sampling was performed at the workers' positions when they were pushing the hot coke and charging the coking coal. After the pushing and charging activities, samples were collected on the topside and coal bunker till the next pushing. Each sampling cycle consisted of collecting air samples during pushing, charging, and coking, and four sampling cycles were conducted every day for 7 days. In the meantime, air samples were collected in the plant areas and sites located at coke oven sides, bench sides, and tar distillation, each being ~3 m away from the coke ovens. The sampling time was 15 min per sample. The inlet for every sample was in the inhalation area and at a height of 1.4 m.

VOCs in the air samples were collected using the commercial 7″ × 1/4″ Tekmar stainless steel multisorbent tubes (Tekmar Company, USA) packed

Table 1 Basic information about the investigated coke plants

Parameter	Plant A	Plant B
Long×wide×height of ovens (m)	11.2×0.42×2.8	15.98×0.5×4.3
Oven battery (N)	25×2	72×2
Coking time (h)	17.0	20.5
Coal charge per oven (t)	11.0	26.0
Technique of coal charging	Top charging	Stamp charging
Coke quenching method	Water	Water
Air pollution control	None	Bag house
Annual output (Ton)	150,000	1,200,000

with Tenax TA and Carbosieve S-III. Air samples were drawn through the sorbent tubes by an attached portable pump (the air flow rate was set to 100 ml min^{-1}) (Air-Check-52, SKC Inc., USA). Before each sampling, the tubes were baked at 230 °C with a flow (40 ml min^{-1}) of ultra-pure helium (99.999 %) passing through and no target compounds were detected by GC/MS. To increase the VOC trapping capacity, two tubes were connected in series. In addition, a tube filter contained silicone-treated glass wool was connected to the front of the tube to remove any particulate matter. After each sampling, the tube was sealed immediately, stored in dark at 4 °C, and analyzed within 7 days.

Chemical analysis

The protocol of US EPA TO-17 was followed for the analysis of VOCs. VOCs were analyzed via a thermal desorption system (Tekmar 6000 Aero Trap, Tekmar Company, City, State, USA) coupled with a Hewlett-Packard Model 5890 gas chromatograph/5972 mass selective detector (HP 5890 GC/5972 MSD). The sampling tubes were thermally desorbed for 20 min at 250 °C with a flow (40 ml min^{-1}) of ultra-pure helium (99.999 %), and the desorbed VOCs were preconcentrated by the trap at 40 °C. In the end, the trap was thermally desorbed at 250 °C for 4 min, and VOCS were transferred to HP 6890 GC and detected by 5973 MSD. The compounds were separated by an HP-VOC capillary column (60 m×0.32 mm id×1.8 mm film thickness) with ultra-pure helium as the carrier gas. The oven temperature was programmed as follows: initial temperature was set at 40 °C for 2 min and then increased at a ramp of 5 °C min^{-1} to 220 °C, which was held for 5 min. The electron ionization (EI)-based MSD was operated in the data acquisition mode of scan, and the mass range was set to 35–300 amu. The method detection limit was ≤0.1 ppbv, duplicate precisions were within 10 %, and the intra-and inter-day detection variation was monitored by the same standard samples and lower than 10 %. A Supelco Calibration Mix was used for establishing external standards calibration, and standard gas mixtures (1.0 ppm) were diluted with zero air, then sampled, and analyzed under identical conditions to those for the field samples. The seven-point calibration (0.0, 1.0, 5.0, 10.0, 50.0, 100.0, 200.0 ppbv) was performed for quantifying the VOCs in the air samples, and the correlation coefficients (*r*) for stand curves were ≥0.99 for all objective compounds. Compounds were identified by their retention times and their mass spectra. M-xylene and p-xylene were co-eluted in the GC columns, and their concentrations were reported as total concentration of the two compounds combined as usually is the case (Wang et al. 2002).

Results and discussion

BTEX levels

In all samples, benzene, toluene, ethylbenzene, and xylene (BTEX) were the most detected VOCs. Considering that the exposure time and levels vary during the whole shift, the coke workers' exposure to BTEX was expressed in the form of time-weighted average (TWA) concentration,

$$C = \sum C_i t_i \Big/ \sum t_i \tag{1}$$

where C_i is the concentration level detected for different working activities i and t_i is the duration of the activity.

Table 2 presents the TWA concentrations of BTEX at the topside of coke ovens and selected plant areas during a typical coking circle. The 8-h TWA concentration levels of benzene, toluene, ethylbenzene, m,p-xylene, and o-xylene at the oven topside were 705.6, 594.6, 24.1, 39.3, and 23.1 μg m^{-3} for plant A and 290.4, 54.4, 3.8, 110.1, and 35.0 μg m^{-3} for plant B, respectively, which were 2.4, 5.5, and 6.0 times higher for benzene, toluene, and ethylbenzene in plant A than plant B. This can be ascribed to the fact that there was no COE control practiced in plant A. A central dust catcher and desulfurizer station were operated in plant B, but some gaseous pollutants, especially VOCs, were not eliminated, which they have been emitted by a chimney 24 m high and decreased the BTEX levels in topside ports. However, in the plant area, the benzene concentrations were quite comparable, with a TWA level of 112.7 and 124.6 μg m^{-3}, and a peak value of 298.4 and 302.0 μg m^{-3} for plants A and B, respectively. VOCs sampled in these plant areas can be affected by the dispersion of COE from oven doors and combustion of hot coke when it was transferred to the quenching tower. And, the emission from by-product processing may be partially responsible, too. The modestly higher BTEX levels in the plant area of plant B can be attributed to its higher output per coke oven, though non-proportional.

Table 2 Concentration levels of benzene, toluene, ethylbenzene, and xylene (BTEX) at the topside of coke ovens and plant areas (μg m^{-3})

Compound	Topside		Plant area	
	A (*c*=27) Mean±standard deviation (range)	B (*c*=28) Mean±standard deviation (range)	A (*n*=20) Mean±standard deviation (range)	B (*n*=22) Mean±standard deviation (range)
Benzene	705.6±259.7 (268.3–1197.7)	290.4±111.2 (85.4–489.7)	112.7±105.0 (21.4–298.4)	124.6±92.7 (14.4–302.0)
Toluene	294.6±196.6 (37.1–503.3)	54.4±28.0 (20.6–98.7)	27.3±23.2 (5.9–79.1)	8.8±5.3 (0.8–18.2)
Ethylbenzene	24.1±15.3 (2.0–44.4)	3.8±3.4 (1.3–8.3)	23.3±19.7 (1.7–57.5)	1.6±2.3 (0.4–7.5)
M,p-xylene	39.3±20.1 (1.2–77.4)	110.1±111.2 (13.0–286.1)	115.4±152.7 (11.8–381.3)	14.2±13.9 (2.1–43.4)
O-xylene	23.1±12.6 (3.0–56.8)	35.0±40.5 (2.6–81.4)	42.7±66.0 (1.5–172.2)	4.0±5.4 (0.4–15.0)

c cycle (includes charging, coking, and pushing phase), *n* sample number

Benzene was the most predominant component of BTEX in the air samples, accounting for 66.8 % (32.7–86.5 %) of the total BTEX, which was in accordance with the reported data in literatures (e.g., Bieniek et al. 2004; He et al. 2005). Being a known carcinogenic air pollutant, benzene has been regulated by a number of agencies in USA and China (Table 3). The 8-h TWA benzene concentrations in samples of the topside and plant areas were below the OSHA limit of 1 ppm and the American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV) of 0.5 ppm TWA. However, 90.0 and 37.5 % of the TWA benzene concentration in the topside samples of plants A and B exceeded the 8-h TWA limit of 0.1 ppm by National Institute for Occupational Safety and Health (NIOSH). The Chinese MEP set a benzene concentration limit of 0.5 mg m^{-3} in the ambient air 10 m away from any source area. The TWA of benzene prescribed by Chinese Ministry of Health was 6 mg m^{-3} (or 1.538 ppm), which is much higher than those regulated by OSHA, ACGIH, and NIOSH. As the Chinese standards are not specifically for coking industry, they were not used as the reference levels in this work; in fact, they have been often used for indoor benzene exposure assessment for industries involving heavy uses of organic solvents such as shoemaking (Wong 2002).

Table 4 lists the benzene levels in coking plants or surrounding areas in different countries. Kivistő et al. (1997) reported that the average concentration of all samples in the Estonian shale oil petrochemical plant was 4.3 times higher in winter than in autumn. COE exposure varied with job categories and locations. The highest aromatic hydrocarbon exposure was found at coke ovens and tar distillation plants, whereas the lowest exposure was at the coke batteries in Upper Silesia, Poland, where benzene concentrations were 3.36 and 0.45 mg m^{-3}, respectively (Bieniek 1998). The average benzene concentration of the coke plant in the Annaba steel complex in France was seven times higher than the regulatory level, with the peak concentration occurring at the laboratory, where the benzene level was ten times higher than the regulatory level (Djafer et al. 2007). A study of benzene exposures of workers in China, who were involved in activities of intensive solvent usages

Table 3 Benzene exposure limits in USA and China

Organization	Levels
Occupational Safety & Health US Department of Labor Administration (OSHA)	TWA 1 ppm STEL 5 ppm
American Conference of Governmental Industrial Hygienists (ACGIH)	TLV-TWA 0.5 ppm STEL 2.5 ppm
National Institute for Occupational Safety and Health (NIOSH)	TWA 0.1 ppm STEL of 1 ppm
Ministry of Health, People's Republic of China	TWA 6 mg m^{-3} STEL 10 mg m^{-3}

1 ppm=3.19 mg m^{-3} at 25 °C and 1 atm

TWA time-weighted average, *STEL* short-time exposure limit, *TLV* threshold limit value

Table 4 Benzene exposure levels in different working areas and surrounding areas of coking plants in different countries

Location	Sampling time	Benzene levels	References
Kohtla-Jarve, Estonia	Winter and late summer 1994	Cokery, 1.3 (winter) and 0.3 $cm^3\ m^{-3}$ (autumn) Benzene factory, 1.6 (winter) and 0.8 $cm^3\ m^{-3}$ (autumn)	Kivistő et al. (1997)
Upper Silesia, Poland	The summer months of 1997	Coke batteries 0.45 $mg\ m^{-3}$ Sorting department 2.03 $mg\ m^{-3}$ Distillation department 3.36 $mg\ m^{-3}$	Bieniek (1998)
Wuhan, China		Top of coke oven 27.2 $\mu g\ m^{-3}$ Mechanical plant of the same factory: ND	Xiao et al. (2002)
Germany	March and May 2000.	Personal benzene levels: Duisburg North 1.5–13.5 mg/m^3; Borken 1.05 $mg\ m^{-3}$	Wilhelm et al. (2007)
China	From 1972 to 1987	Benzene occupational exposure <10 ppm	Wong 2002
Cornigliano, Northern Italy	1998–2002	20.1 (1998), 10.8 (1999), 18.5 (2000), 18.4 (2001), and 2.7 $\mu g\ m^{-3}$ (2002) after close	Parodi et al. (2005)
Upper Silesia, Poland	Summer of 2001 and 2002	Tar distillation department 352.0 ppb Oil naphthalene distillation department 129.4 ppb	Bieniek et al. (2004)
UK		0.07 to 0.28 ppm 8 h TWA	Colman and Coleman (2006)
Annaba, French	December 2004	Total cookery 7.35 ppm Gas and by-product treatment unit 6.8 ppm Laboratory 12.03 ppm	Djafer et al. (2007)

such as painting, printing, shoemaking, and chemical industries, suggested that the average level of benzene exposure ranged from several milligram per cubic meter to 2000 $mg\ m^{-3}$ (Wong 2002). Compared with those reported results, the benzene exposure levels in this study were lower than the solvent-intensive industries, but higher than the coking counterparts, especially for plant A that had a relatively small output (150,000 t coke per year). Researchers also reported that COE on the topside of coke ovens in Shanxi Province, China, PM, and BaP levels decreased with a higher oven capacity (Li 2000; Qian et al. 2006). By 2009, the CNDRC had released 186 coking plants that were considered in compliance with the Admittance Conditions of Coking Industry, and 80 % of the coking plants had a coke oven height of 4.3 m or higher.

Effect of coking activities

Our data reveal that high COE exposure levels at the topside of coke oven were related to coking activities during coke production. Larry car operators, lidmen, and door machine operators stationed very close to the oven were exposed to volatiles released from the topside and side during charging and pushing and, thus, showed the highest mean breathing zone concentrations. Intermediate exposure to the volatiles was for those on the coke side, where workers are exposed through door leakage but are able to move away during the pushing operation. The lowest exposure was for the pusher operators or those who do not work near the coke ovens. Data compiled by IARC and other reports indicated that the average exposures to COEs in the breathing zones were the lowest for the pusher machine operators and highest for lidmen, tar chasers, and Larry car operators (IARC 1984; Chen et al. 1999).

The BTEX monitoring at the topside of ovens for both plants A and B showed the highest exposure during charging, followed by pushing and the lowest during coking. The concentration of benzene was 4.19 and 1.76 times higher during charging and pushing, respectively, in plant A, than that during the coking process, compared to 2.56 and 1.44 times higher, respectively, in plant B. Compared with the NIOSH thresholds, all samples in plant A and 50 % samples in plant B exceeded the 0.1-ppm (TWA) limit. Figure 2 presents the range of BTEX variation in the air of the coke oven topside in plant B. The geometric mean of benzene concentrations and the range were 198.7 (85.4–361.4), 286.8 (245.1–297.5), and 508.4 $\mu g\ m^{-3}$ (327.2–689.7) for the coking, pushing, and charging processes, respectively. Evidently, the peak exposure to coke oven workers occurred during charging and pushing. Consequently, COE control should focus on controlling emissions during charging and pushing.

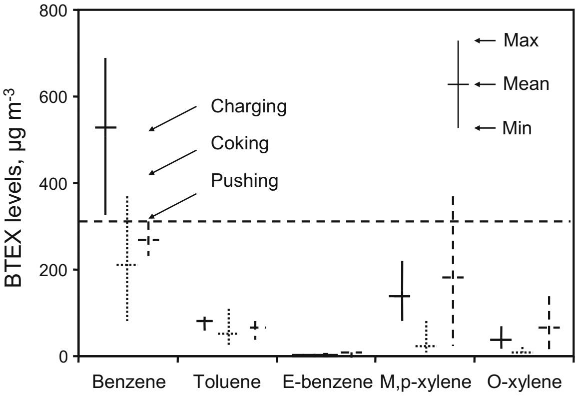

Fig. 2 Range of BTEX at the topside of coke oven during charging, coking, and pushing in plant B (μg m^{-3})

The BTEX levels were higher in the area surrounding the coke oven than those of the more distant sampling locations. The highest benzene concentration near the coke oven was 298.4 μg m^{-3} in plant A and 302.0 μg m^{-3} in plant B. And, the lowest concentration was 21.4 and 14.4 μg m^{-3}, which was detected at the boundary of plant A and at the coal preparation sites of plant B, respectively. Figure 3 presents the distribution of BTEX surrounding the coke oven and at the tar distillation sites in plant B. BTEX concentrations were higher at the coke side (>3 m) than those at the push side and tar distillation area. Benzene concentrations at the tar distillation were 73.1 μg m^{-3}, ranging from 14.4 to 138.3 μg m^{-3}. The chemical compositions were similar to those of the coking process, indicating that leaking of coal gas from the tar distillation can greatly affect the benzene levels in plant areas. It has been reported that approximately 60 % of the total emissions occur during charging, 30 % during pushing, and 10 % during quenching (Kirk-Othmer 1979). Based on benzene emission data at a coking plant in Germany, Reeve (2000) estimated the following allocations, 39 % from charging holes, 28 % from oven doors, 18 % from ascension pipes, and 13 % from charging and leveling . Measurements at an old 4.5-m battery showed that 48 % of the PAHs and BTEX emissions came from the oven doors and 42 % from the charge hole lids (Sloss 2001). Both literature data and the fact that 52 % of benzene in plant B was from the coking process suggest that from a COE emission control standpoint, while COE from charging and pushing should be focused, diffusion/dispersion from tar distillation should also be considered.

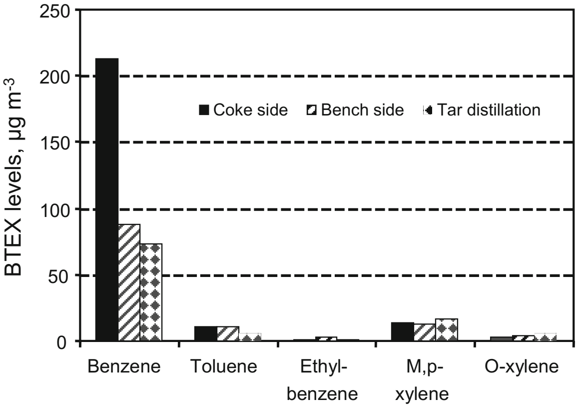

Fig. 3 Distribution of BTEX at coke side, bench side, and tar distillation in plant B (μg m^{-3})

Risk assessment

The health risk of a carcinogen is often quantitatively assessed based on the dose of an agent and the likelihood of a carcinogenic effect. The exposure (*E*) for an individual chemical (*i*) due to intake processes (inhalation and ingestion) can be calculated via Eq. (2) (US EPA 1998),

$$E_i = C_j \ \mathrm{IR}_i \ t_{ij} \tag{2}$$

where *C* is the concentration of the pollutant (μg m^{-3}), IR is the inhalation rate (m^3 h^{-1}), *T* is the exposure time (h day^{-1}), and *j* is the corresponding micro-environmental system.

For benzene exposure, the inhalation unit risk is reported as a range, from 2.2×10^{-6} to 7.8×10^{-6} per microgram per cubic meter (US EPA 1998). Based on the standard air intake factor of 20 m^3 day^{-1}, the standard body weight of 70 kg, and the absorption factor of 50 %, the exposure risks for workers on the coke oven topside and in the plant areas are calculated and are shown in Table 5. The average benzene doses at the topside and in the plant area were, respectively, 33.6 and 5.4 μg kg^{-1} day^{-1} in plant A and 14.2 and 5.9 μg kg^{-1} day^{-1} in plant B. Based on the exposure time and level, the percentages of benzene exposure were estimated to be 31.4 % from charging, 24.4 % from coking, and 44.2 % from pushing in plant A and 35.0, 31.7, and 33.3 %, respectively, in plant B (Fig. 4). Charging and pushing activities accounted for nearly 70 % of benzene dose owing to their contributions to the peak concentrations at the topside.

The 8-h benzene exposure risks to the coke oven workers were calculated to be 7.4×10^{-5}–2.6×10^{-4} for

Table 5 Comparison of exposure risks of benzene at the topside of coke ovens and coke plant areas (μg/kg/day)

Parameter	Topside				Plant area			
	Airth. mean	95th percentile	Risk		Airth. mean	95th percentile	Risk	
			Mean	95th percentile			Mean	95th percentile
A	705.6	915.5	7.4×10^{-5}–2.6×10^{-4}	9.6×10^{-5}–3.4×10^{-4}	112.7	283.5	3.1×10^{-5}–1.1×10^{-4}	4.0×10^{-5}–1.4×10^{-4}
C (μg m^{-3})	33.6	43.6			5.4	13.5		
E (μg kg^{-1} day-1)								
B	298.2	385.2	1.2×10^{-5}–4.2×10^{-5}	3.0×10^{-5}–1.0×10^{-4}	124.6	286.9	1.3×10^{-5}–4.7×10^{-5}	3.0×10^{-5}–1.1×10^{-4}
C (μg m^{-3})	14.2	18.3			5.9	13.7		
E (μg kg^{-1} day^{-1})								

plant A and 1.2×10^{-5}–4.2×10^{-5} for plant B. Considering one-eighth coke production in plants A to B, the benzene risk was 49.3 times in plant A than that in B. Based on data from epidemiological investigation of coke oven workers, US EPA (1984) reported a proper risk range of from 1.30×10^{-8} to 1.26×10^{-3}, with the best point estimate being 6.17×10^{-4} for the continuous COE exposure from birth (US EPA 1984). Moolgavkar et al. (1998) estimated that the unit risk of COE was 1.5×10^{-4} with a new method based on the two-stage clonal expansion model of carcinogenesis. Compared with these risk data, Chinese coke workers were at a higher cancer risk. Based on the production capacity of 393 t coke per coke worker per year (Chen and Polenske 2006), the population of Chinese coke workers was as high as 8.6×10^{5} in 2006. Furthermore, the coke plants were concentrated in the northern China and heavily populated regions. Consequently, the health impacts are substantial and widespread, and thus, it is imperious to take measures to curb the health risks associated with the COE exposure.

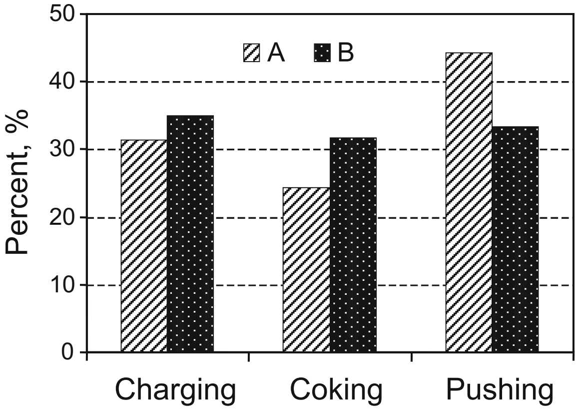

Fig. 4 Percentage of lifetime cancer risk at the topside of coke oven during the coke production

Implications to the environment at large

COE is not only hazardous to coke oven workers, but also dispersible to the surrounding atmosphere. A gradient of smog-like air pollutants was observed around the coke oven of plant A, which disappeared or dropped after its closing. Parodi et al. (2005) reported that the benzene concentration in the ambient air near Cornigliano, Italy, decreased from 10.8 to 20.1 μg m^{-3} in 1998–2001 and to 2.7 μg m^{-3} in 2002 upon closing several coke plants in selected locations. Federico et al. (2005) reported that high concentrations of BaP (annual mean 8 ng m^{-3}) and benzene (annual mean 15 μg m^{-3}) in an industrial area in Genoa, Italy, decreased significantly (BaP 0.2 ng m^{-3}, benzene 2 μg m^{-3}) following the coke oven closure. Based on these results, the heavy coke production in the northern China at least partially contributes to the high levels of particulate matter and other pollutants in northern Chinese air, which is in accordance with a report by the MEP of People's Republic of China (MEP 2004–2012).

The monoaromatic hydrocarbon ratios have been used as indicators of emission sources or atmospheric age (e.g., Nelson and Quigley 1984). Table 6 presents the average benzene ratios relative to toluene, ethylbenzene, and xylene (by weight) in different air samples. A B/T ratio of around 0.5 compared with B/E (>1) and B/X (<1) has been reported to be characteristic of petroleum-related sources such as gasoline and vehicle emissions (e.g., Schauer et al. 1999; Wang et al. 2002; Qiao 2011; Zhang et al. 2013). For burning biofuel, charcoal, and coal, it is typical that the B/T ratio is higher than 1, B/E higher than 10, and B/X ranging from 1 to 10 (Andreae and Merlet 2001; Schauer et al. 2001; Tsai et al. 2002; Moreira dos Santos et al. 2004; Wang et al. 2014). In this study, the B/T ratios in all samples were

Table 6 Comparison of average benzene ratios relative to toluene, ethylbenzene, and xylene (by weight) in different air samples

Sources	Items		B/T	B/E	B/X	References
Coking area	A	Charging	1.9	47.1	8.6	This work
		Coking	2.6	16.3	15.9	
		Pushing	3.4	32.3	14.4	
		Plant area	4.3	4.8	0.7	
	B	Charging	6.7	148.6	2.6	
		Coking	3.2	63.2	4.3	
		Pushing	8.8	59.9	1.1	
		Plant area	17.7	77.1	6.8	
Diesel engine			0.7	5.8	0.9	Schauer et al. (1999).
Vehicle emission	Gasoline vehicle		0.4	0.7	0.2	Qiao (2011)
	LPG motor vehicle		0.8	1.0	0.4	
	Diesel engine		1.1	3.6	1.2	
Gasoline evaporation			0.2–0.5			Zhang et al. (2013)
Tunnel air	Tunnel air		0.7	3.3	0.7	Wang et al. (2002)
	Gasoline		0–0.3	0.3–1.3	0–1.4	
Biomass burning	Savanna and grassland		1.8	17.7	5.1	Andreae and Merlet (2001)
	Tropical forest		1.6	16.7	6.7	
	Extratropical forest		1.2	10.2	2.5	
	Straws of rice, wheat, bean and rape, and wood		1.7			Wang et al. (2014)
Wood combustion	Pine		2.4	16.7	4.9	Schauer et al. (2001).
Power station	Stack gas		8.5	32.9	55.5	Moreira dos Santos et al. (2004)
	Surroundings (VM)		2.5	10.8	2.7	
House stove			2.0–39.2	16.5–	1.5–	Tsai et al. (2002)
Northern China	Taiyuan		1.1			Barletta et al. (2005)
	Shijiazhuang		1.2			
	Changchun		1.4			
Megacity	Beijing		0.76			Duan et al. (2008)

3.05 (1.9–4.3) for plant A and 9.1 (3.2–17.7) for plant B; B/E ratios were 25.1 except for those from area of plant A (4.8), and B/X ratios ranged from 1 to 20. Evidently, the BTEX compositional profiles of COE differ greatly from those of petroleum-related sources, whereas the B/E and B/X ratios partially matched that for typical biofuel, charcoal, and coal. The higher B/T ratio showed the unique characteristics of COE compared to other reported emission sources.

The BTEX ratios were also used for source analysis in ambient air monitoring in various cities (e.g., Monod et al. 2001; Liu et al. 2009). It was reported that vehicular emissions are the main source of VOCs in some megapolis such as New York, London, Tokyo, and Beijing, etc. Barletta et al. (2005) reported that the primary VOC source in 43 major Chinese cities was gasoline combustion or evaporation, but the type of combustion responsible for non-methane hydrocarbon (NMHC) emissions was not clearly identified, especially in northern China. Compared with traffic-related cities, B/T ratio in some northern cities (e.g., Taiyuan, Shijiazhuang and Changchun) was higher than 1 (Table 6), meaning that coal-related emission had a great contribution for VOCs in these cities (Barletta et al. 2005). Duan et al. (2008) found that the B/T ratio was 0.76±0.21, which suggests that vehicular emissions were not the only main source of VOCs in Beijing. Based on the distribution of coke plants and coke production in China (Fig. 1a), coke production can be a great contributor to the heavy air pollution in northern China, where is the major coke production base in China, accounting for 60 % of total coke production in China (Yang et al. 2006). Future work must be done for the VOC emission profile by coke production, which then can be used in the positive matrix factorization (PMF) and estimated the coke production contribution to the atmospheric VOCs in northern China.

Conclusions

This work presents first-hand field data on the VOC emissions from typical Chinese coke plants in Shanxi Province where coking has been heavily practiced for decades and assesses the associated exposure and health risks to coke workers. The TWA concentrations of benzene were 705.6 and 290.4 $\mu g\ m^{-3}$ in plant A and plant B, respectively, which were higher than those reported in other countries. Peak COE was observed at the topside of coke oven during charging and pushing processes, which constitute the major VOC exposure for the coke workers, and varied greatly with coking activities and sampling locations. COE dispersion from coking processes also contributed significantly to coke workers' exposure to VOCs. In the pant area, the BTEX concentration was highest at the coke side, followed by the bench side. Benzene exposure from the dispersion of tar distillation should also be concerned. Based on the IRIS risk criteria, Chinese coke workers were of high cancer risks. The B/T ratios in all samples showed a different characterization from other emission sources, and COE is at least partially responsible for the high VOC concentrations in northern Chinese air. Given the limited field data on COE from Chinese coke plants, the results provide some baseline risk data for assessing potential VOC exposure in Chinese coking plants.

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