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Environmental Risk Presented by Arsenic Contamination of Building and Facility Surfaces in a Coking Plant

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Abstract Arsenic contamination on the surface of buildings and facilities at a coking plant and associated health risk were studied. A total of 94 wipe samples from 56 buildings and facilities were collected, and As concentrations were found to range from 0.01 to 23.90 μg/100 cm^2. 20.2% of the samples exceeded the As level calculated to present health risk: 4.02 μg/100 cm^2. Arsenic mean concentration was found to be highest on the surface of bricks, and coking zone showing the highest As risk. The findings of this study may provide clues to As pollution control and risk evaluation in coking plants.

Keywords Arsenic · Coking plant · Risk screening level · Assessment

Arsenic (As) is the first metallic element identified as carcinogenic (Hutchinson 1888) and increase in its concentration can disrupt the normal functions of the ecosystem and pose risks to plants, animals, and humans (National Research Council 1997). Arsenic contamination has become a worldwide environment and health problem, and in recent years, public concern regarding this element has increased due to the recent incident of chronic As poisoning caused by contamination in Bangladesh, China and West India (Nordstrom 2002; Liao et al. 2005). Nriagu and Pacyna (1988) estimated that globally about 9.4×10^8 kg of As is emitted into the soil every year, including 23.0% from coal ash and 14.0% from atmospheric dust fall.

The process of coking, using coal as the raw material, could lead to As contamination and bring adverse effects on human health and environment (Cangialosi et al. 2005; Yudovich and Ketris 2005). Arsenic has a strongly affinity to coal and may be present in it either organic or inorganic (FeS_2As, As_2S_3) forms (Yudovich and Ketris 2005; Barraj et al. 2006). Various operations during the coking process can generate As-rich coal dusts and airborne particles suspending in the atmosphere around the plant and can precipitate onto the surfaces of buildings and facilities (Wang et al. 2010; Zeng et al. 2001; Nelson 2007). After precipitating on buildings and facilities, As may enter the human body through two routes: direct body contact and subsequent absorption via the skin (dermal absorption route) (Tang 2003), or via hand contact followed by transfer to the mouth and intake through the digestive system (dermal-to-oral route). Upon entering the human body, As is rapidly carried by the circulatory system throughout the body and subsequently affects the host's health. It has been well recognized that certain daily products including wood board, picnic tables and chairs and entertainment facilities, etc. were commonly made of CCA (Cu–Cr–As)-treated wood and the toxic residues of As on the wood products would have negative effect on children health through ingestion pathways (Barraj et al. 2006; Dang et al. 2003). After the American 9.11 events, the local department of public health and environmental protection demonstrated that contaminants such as As containing in the dust of building waste would adhere to the building surfaces, which might pose great risk to human health (US EPA 2003). Up to date, research concerning with the As pollution survey on building surfaces are scarce to report.

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A large comprehensive coking plant in Beijing city, China was moved out at the year of 2007, and part of the plant is planning to be a large industry heritage park. The coking plant (built in 1958 and operational since 1959) mainly produces coke and coke oven gas, but more than 40 other chemical products such as tar, benzene, ammonium sulphate, asphalt, and naphthalene are also produced. The original industrial structures, including 94 buildings and production facilities (e.g. large gas tanks, cooling towers, primary gas coolers, crude benzene scrubbers, and coke-pushing ovens), are planned to be kept. However, whether the reserved buildings could bring some health risk or not is unclear. The plant has more than 50 years of production and construction history, and was mainly responsible for the production of pipeline gas. Our previous investigation in this plant found that the As concentration in the soil surface layer (0–1 m) reached 499 mg/kg, indicating a severe As contamination. In this work, we analyzed the As concentrations in samples collected from the surfaces of buildings and facilities. Our objectives were to: (1) determine the distribution of As on these surfaces, (2) reveal the characteristics of As contamination on the surfaces in various functional zones and materials, and (3) evaluate the health risk associated with As contaminations.

Materials and Methods

Fifty-six sampling sites (Table 1) in various zones of the plant were selected and their coordinates were recorded using a global positioning system (GPS) (Fig. 1). A total of 94 wipe samples were collected from the surfaces of buildings and production facilities at these sites. Additionally, control wipe samples of glass, antirust paint, cement, and brick surfaces were collected in an office park 25 km northwest-direction away from the plant.

Surfaces in the coking plant and control zone were sampled by wiping (US EPA 2003). A piece of gauze (7.5 cm × 7.5 cm) was moistened with deionised water and used to wipe a 10 × 10 cm area of the target surface. The sample information was recorded and the gauzes were labelled and kept in sealed plastic bags (US EPA 2003, 2007). Each time another gauze without wiping the surface was moistened and preserved in the same manner as control sample.

The gauzes were each transferred into a conical flask and digested with HNO_3–H_2O_2 over a hot-plate. The resulting solution was then transferred in a 50 mL volumetric flask and the volume adjusted with ultrapure water. The same volume of HNO_3–H_2O_2 digestant served as the control for analyses. The As concentrations in the solutions were analyzed with a dual-channel atomic fluorescence spectrophotometer (AFS-9130, Beijing Jitan Instruments) (Liao et al. 2005).

All reagents used were GR grade and ultrapure water was used. All glassware was immersed in a HNO_3–H_2O (1:5) solution overnight, then washed with tap water and finally rinsed with deionised water three times before use. All sample transportation and storage was conducted in a temperature controlled environment at a consistent temperature of 4°C.

An evaluation method presented by the US EPA was used to calculate the risk associated with As contamination of surfaces (Dibiasio and Klein 2003). Given the carcinogenicity and non-evaporative properties of As, only dermal-to-oral and direct dermal absorption routes were investigated in this study. The equations are as follows:

$$C_{\mathrm{wipe}} = \frac{\mathrm{RISK} \times \mathrm{UCF} \times 100\,\mathrm{cm}^2/\mathrm{wipe}}{\mathrm{CSF} \times 2 \times [(\mathrm{ABSder} \times \mathrm{cCNSTder}) + (\mathrm{cCNSTing})]} \tag{1}$$

where

$$\mathbf{c}\mathrm{CNSTder} = \frac{\mathrm{SAd} \times \mathrm{CF} \times \mathrm{TE} \times \mathrm{EF} \times \mathrm{ED}}{\mathrm{BW} \times \mathrm{ATc} \times \mathrm{UCF}} \tag{2}$$

$$\mathbf{c}\mathrm{CNSTing} = \frac{\mathrm{SAi} \times \mathrm{CF} \times \mathrm{TE} \times \mathrm{fdo} \times \mathrm{fgi} \times \mathrm{EF} \times \mathrm{ED}}{\mathrm{BW} \times \mathrm{ATc} \times \mathrm{UCF}} \tag{3}$$

The level of As deemed hazardous for children was used as the parameter for this study because children are more sensitive to toxic substances such as As and therefore experience the highest risk (Dibiasio and Klein 2003). Parameters used in the evaluation are listed in Table 2, and the risk associated with As-contaminated surfaces was calculated (using Eq. 1) to be 4.02 μg/100 cm^2.

Data were analyzed with SAS. Plots were drawn with OriginPro 7.5. Contour maps were drawn with ArcGIS 9.0.

Results and Discussion

Park is one of important site for living and amusement, As contamination of the surfaces of buildings and facilities kept in the industry heritage park is associated with a potential hazard to human health. Table 3 summarizes the statistical information of As concentrations on the surfaces of buildings and production facilities. The As concentrations in 20.2% of the 94 surfaces samples exceeded the level calculated to present a health risk to humans: 4.02 μg/100 cm^2. For different function zones, 26.3% of the wipe samples collected from the coking zone exceeded the maximum acceptable level, compared with 25.0% from the refinery zone, 14.3% from the gasification zone, and none from the office and living zone.

Location of buildings and facilities is one of major factors that affects As contamination of surfaces, and it can

Table 1 Detail information of sampling sites

No	Information of sampling site	Surface sampled	Functional zone
1	Boiling house	Brick, glass, antirust paint	Coking
2	Coke-quenching tower	Brick	
3	Old central screening building	Cement	
4	Old coal blending building	Brick	
5	Coke-pushing oven	Coating, glass	
6	Car dumper building	Cement, glass	
7	Raw coal warehouse	Cement	
8	Coal blending building	Cement	
9	Coke-pushing cart	Antirust paint	
10	Coke storage building	Cement	
11	East primary cooler	Antirust paint, coating, aluminium	Refinery
12	Ventilator house	Glass, antirust paint	
13	Cooling pump house	Glass, cement, brick	
14	Cement post	Cement	
15	Oil warehouse	Brick	
16	Desulfurizer	Antirust paint	
17	Desulfurization-ammonia distillation pump house	Coating, glass, wood, antirust paint	
18	8-m water cooling refinery tower	Cement	
19	Combustion furnace	Antirust paint	
20	Benzene stripping tower	Antirust paint	
21	Crude benzene storage tank	Hard sponge	
22	Brick wall	Brick	
23	Brick building	Brick	Gasification
24	Ground-mounted compressed spiral wet gasholder	Antirust paint	
25	Brick wall	Brick	
26	Desulfurization tower	Antirust paint	
27	Cement post	Cement	
28	Warehouse	Glass	
29	Cement post	Cement	
30	Main gas producer house	Gypsum, glass	
31	Desulfurization and recovery building	Brick	
32	Desulfurization and recovery facility	Cement, antirust paint	
33	Warehouse	Cement	Office and residence
34	Brick building	Brick	
35	Supporting pillars	Antirust paint	
36	Supporting frame	Antirust paint	
37	Carbonization division building	Marble, glass	
38	Brick wall	Brick	
39	Cafeteria of the coking plant	Ceramic tiles	
40	Single-storey building	Coating	
41	Main office building	Glass, wood, cement	
42	Supporting pillars	Antirust paint	
43	Quality check building	Ceramic tiles, glass	
44	Office building	Brick	
45	Cement post	Cement	
46	Maintenance workshop	Brick	Others
47	Sludge dehydration building	Brick	
48	Aeration tank	Cement	
49	Pre-coagulation de-oiling tank	Cement	
50	Desulfurization recovery facility	Antirust paint, iron	
51	Production building	Glass	
52	Brick building	Brick	
53	Brick building	Brick	
54	Cement post	Cement	
55	Cooling recycle tower	Cement	
56	Cement post	Cement, iron	

be seen from Table 3 that the concentrations on these four types of functional zones varied widely. The mean As concentration on the surfaces of buildings in the coking zone was 4.65 μg/100 cm^2, which is 15.6% higher than the maximum acceptable level, while those in the refinery, gasification, and office and residence zones were all below the maximum acceptable level. Statistical analyzes revealed that the As concentrations on the surfaces of buildings and facilities in the coking zone were significantly higher than those in the other four functional zones. Therefore, the coking zone presents the highest risk to human health. Coking zone is primarily responsible for the production of coke, and coking includes complex processes and generates a range of by-products, therefore, buildings and facilities in this zone would have more exposure to coal, coal dust and As-containing fumes and particles

Fig. 1 Schematic graph of sampling sites, the *numbers* in the figure represent the numbers of sampling sites

Table 2 Exposure parameters for children

Parameter	Abbreviation	Value	Unit	Reference
Skin surface area	SAd	3,200	cm^2	US EPA 1997
Skin surface area, ingestion	SAi	390	cm^2	US EPA 1997
Contact frequency	CF	8	Events/day	Michaud et al. 1994; Paull 1997
Surface-to-skin transfer efficiency	TE	0.1		Paull 1997
Exposure frequency	EF	350	days/year	BMEPB 2009; US EPA 1989
Exposure duration	ED	2	year	BMEPB 2009
Body weight	BW	15	kg	BMEPB 2009; US EPA 1989
Averaging time-cancer	Atc	2,190	days	US EPA 1989
Unit conversion factor	UCF	1,000	μg/mg	
Fraction transferred from dermal-to-oral	fdo	1		Dibiasio and Klein 2003
Fractional GI absorption	fgi	1		Dibiasio and Klein 2003
Target risk	RISK	1×10^{-6}		
Dermal absorption (fraction)	ABSder	0.03		DTSC 1999
Oral cancer slope factor	CSF	1.5	$(mg/kg/day)^{-1}$	BMEPB 2009; IRIS

created by the combustion of coal and the coal-based coking process.

The number of buildings and facilities of which surface As concentrations exceeding the maximum acceptable level (4.02 μg/100 cm^2) was 6 in the refinery zone, which is highest among all functional zones; followed by those in coking zone and the number is 4 (Fig. 2). However, As concentrations of surface samples of buildings and facilities in the office and residence zone was not found exceeding the maximum acceptable level (4.02 μg/100 cm^2). The two buildings found to have the highest average As concentrations (23.9 μg/100 cm^2 at a boiling house and

Table 3 As concentrations on the surfaces of the buildings and facilities distributing in different functional zones

		Functional zone				
		Coking	Refinery	Gasification	Office and residence	Other
Number of samples	94	19	24	14	19	18
Minimum	0.01	0.47	0.01	0.26	0.23	0.33
Maximum	23.90	23.90	7.48	4.76	3.13	22.83
Median	1.72	2.17	2.59	0.85	1.48	2.00
Mean	2.91	4.65	2.74	1.70	1.42	3.81
Standard deviation	4.05	6.67	1.98	1.52	0.87	5.20
Coefficient of variation (%)	139.37	143.49	72.10	89.26	61.49	136.45
Skew	3.97	2.51	0.76	1.07	0.34	3.17
Kurtosis	17.58	5.44	0.01	−0.25	−0.63	11.49

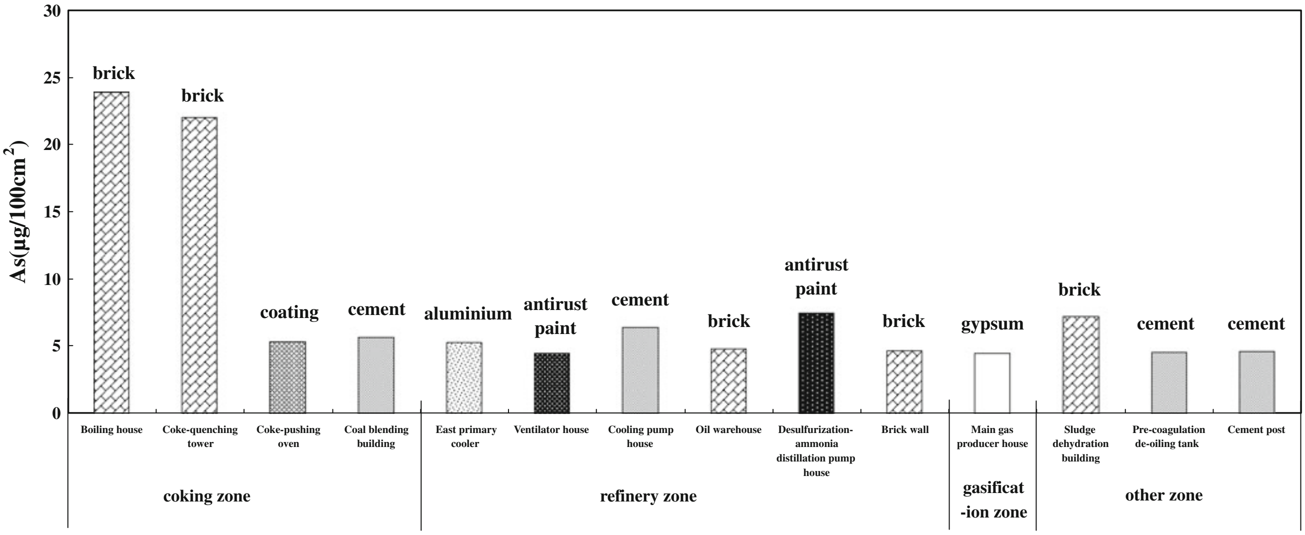

Fig. 2 As concentrations of different surfaces of building and facilities exceeding the maximum acceptable level (4.02 μg/100 cm^2) in different functional zones

22.00 μg/100 cm^2 at a coke-quenching tower) were both in close proximity to the site of coal combustion. Fine particles containing high concentrations of trace elements including As mainly produced from coal combustion (Nelson 2007), and easily trapped in pores on the surface of substrates where they land. Yang et al. (2006) reported that the As concentrations in the dust falling near coking plants was 19.8 times higher than that in control zones.

Glass, antirust paint, cement and bricks represented the most common structural surfaces in this coking plant, and some surface materials, such as hard sponge, gypsum, marble, ceramic tiles, were not very common in the plant and were belong to other materials in the study. The concentrations on these four main types of surface varied widely (Fig. 3). The highest average As concentrations were found on bricks (4.88 μg/100 cm^2), followed by cement (3.38 μg/100 cm^2), then antirust paint (1.71 μg/100 cm^2), and finally glass (0.54 μg/100 cm^2), which were 4.15, 9.5, 21.2 and 11.6 times higher than their counterpart surfaces measured in the control zone, respectively. Statistical analyses revealed that the As concentration on brick surfaces were significantly higher than those on the other three surfaces investigated.

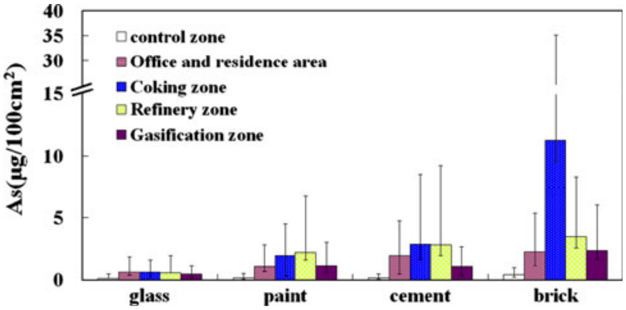

Fig. 3 As concentrations (Average ± (Min, Max)) on the surfaces of the same materials in different functional zones

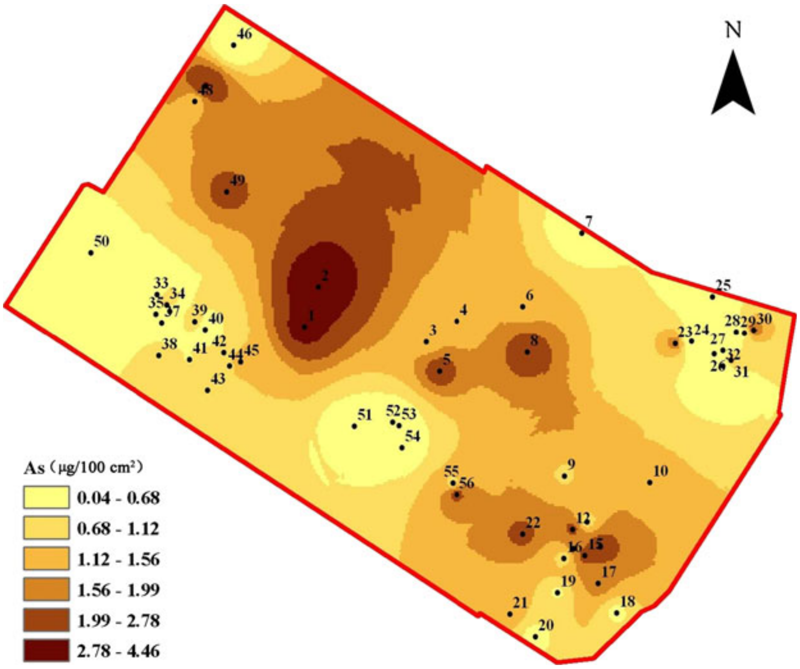

Fig. 4 Geographical distribution of As levels on the surfaces of building and facilities in the plant, the numbers in the figure represent the numbers of sampling sites

The As concentrations on bricks showed the largest variation among the functional zones whereas glass surfaces showed the least variation (Fig. 3). For the surface material of glass, the difference of As average concentrations of different zone was not significant. For painted and cement surfaces, the As average concentrations in the zone of refinery and coking were higher than gasification, office and residence zone. The highest As concentration of the materials of glass, paint, and cement were 1.37, 4.52 and 6.42 μg/100 cm^2, respectively, and all were appearing in the refinery zone. On the bricks, the order of As average concentrations was: coking > refinery > gasification > office and living zone. Statistical analyses revealed that the differences in As concentration among the functional zones were not significant for any surface. Caffrey et al. (1998) observed that the dry deposition of particles depended on the characteristics of the depositing surface, such as roughness, porosity and adsorptive properties. Of the four types of surface studied, 5.6% of the samples collected from antirust paint, 24.0% from cement, and 31.6% from bricks were beyond the maximum acceptable level. The As concentration on bricks in the coking zone (11.24 μg/100 cm^2) was two times higher than the maximum acceptable level, but the concentrations on other surfaces remained below it. It was detected that the material of cement, bricks, and paint made of the surfaces of buildings and production facilities in the plant contained a certain of As, and their concentrations were 10.3, 7.1 and 8.6 mg/kg, respectively. Arsenic effusion from these surface materials may also contribute to the level of As contamination.

Figure 4 shows spatial distribution characteristics of As on the surfaces of buildings and facilities in the coking plant. The concentrations were not normally distributed and thus the logarithms of the concentrations were used for interpolation. It can be seen that As contents on various building surfaces were highly spatially heterogeneous. Several high concentration patches were identified in the plant area, which were located in the middle of the coking division, the boiler house, and near a coking-quenching tower. These As-rich patches were located in a wide swathe running from the northwest to the southeast of the study area, probably because the coal dust emitted from the coking zone was carried by wind to reach the southeast and northwest areas of the plant. Yang et al. (1983) analyzed air-borne particles in the atmosphere at a distance of 30 m from an electric power plant in Tianjin (China) and found a As concentration of 0.062 μg/m^3 in the downwind particles, compared with 0.031 μg/m^3 in the upwind particles, indicating that the downwind surfaces had more exposure to As-containing air-borne particles and coal dust than the upwind surfaces.

The research carried out in the coking plants has documented increasing concentrations of As on the surface of buildings and facilities. A potential health risk assessment associated with contamination of surfaces has been processed base on exposure parameters. It was found that the surfaces of different buildings and facilities present different levels of As contamination risk for the sake of surface materials and distribution locations. Arsenic was shown a substantial buildup with an increase on the brick, the cement, and the paint over the glass. Compared with other functional zones studied, the coking zone appeared to contain the highest content of As. These results suggest that the coking plants possess some hazards to human health, and the surfaces with unacceptable levels of As contamination (e.g. the Coagulation-de-oiling tank, New coal blending building, Sludge dehydration building, Coke quenching tower, Boiler house, Cooling pump house and Coke-pushing furnace) should be cleaned to reduce the risk of this occurring to an acceptable level. Thus cleaning, recycling and other management measures must be carried out to ensure the safe reuse of these facilities for the heritage park.

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