



Arsenic concentrations in Chinese coals

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Abstract

The arsenic concentrations in 297 coal samples were collected from the main coal-mines of 26 provinces in China were determined by molybdenum blue coloration method. These samples were collected from coals that vary widely in coal rank and coal-forming periods from the five main coal-bearing regions in China. Arsenic content in Chinese coals range between 0.24 to 71 mg/kg. The mean of the concentration of Arsenic is 6.4 ± 0.5 mg/kg and the geometric mean is 4.0 ± 8.5 mg/kg. The level of arsenic in China is higher in northeastern and southern provinces, but lower in northwestern provinces. The relationship between arsenic content and coal-forming period, coal rank is studied. It was observed that the arsenic contents decreases with coal rank in the order: Tertiary>Early Jurassic>Late Triassic>Late Jurassic>Middle Jurassic>Late Permian>Early Carboniferous>Middle Carboniferous>Late Carboniferous>Early Permian; It was also noted that the arsenic contents decrease in the order: Subbituminous>Anthracite>Bituminous. However, compared with the geological characteristics of coal forming region, coal rank and coal-forming period have little effect on the concentration of arsenic in Chinese coal. The average arsenic concentration of Chinese coal is lower than that of the whole world. The health problems in China derived from in coal (arsenism) are due largely to poor local life-style practices in cooking and home heating with coal rather than to high arsenic contents in the coal.

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1. Introduction

Coal plays an important role in the energy consumption of China. About 75% of China's energy needs come from coal combustion and this reliance is not expected to change over the

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next several decades. However, coal is not a clean energy. It contains many harmful compounds, such as arsenic and mercury. During mining and combustion, these toxic substances may be transferred to ambient environment and affect human health (Swaine and Goodarzi, 1995; Matschullat, 2000; Finkelman et al., 2002). Arsenic presents a high potential of environmental impacts. The potential arsenic contamination of water, air, and food from coal is a significant environmental health concern (Bencko and Symon, 1977; Zheng et al., 1999; Ng et al., 2002). In Guizhou Province, China, more than 3000 people have suffered from arsenism due to burning high arsenic coal (Zheng et al., 1999). The arsenic contents of many coals can be reduced by up to 70% by cleaning (Finkelman, 1994); however, in 1997, only about 20% of the coal mined in China was subjected to cleaning (Chen, 2001). In many regions in China, raw coals are burned directly.

Although widely distributed in the natural environment, arsenic is generally present in very low concentrations. Concentrations of arsenic in most of coals range from 0 to 80 mg/kg and the mean is 5 mg/kg (Swaine, 1990; PECH, 1980). But some coals contain especially high-arsenics in certain regions in China (Zheng et al., 1999; Ren et al., 1999a,b). Thus, knowing the distribution of As in coal is very important. With respect to production of a clean utility coal, coals of low arsenic content will be most desired because coals with high arsenic contents will have to be cleaned before combustion. The concentration distributions of arsenic in Chinese coals have received much attention (Chen et al., 1989; Ren et al., 1999a,b; He et al., 2002; Zhang et al., 2004). However, their results of the average arsenic content of Chinese coals are not quite precise due to insufficient samples from the limited areas, and a study of more coal samples from larger areas in China is required to obtain a more representative mean value of arsenic in Chinese coals.

In this study, 297 representative coal samples were measured by molybdenum blue coloration method. The average and geometric mean of arsenic in Chinese coals are reported, and the relationships between arsenic content and coal-forming period, coal rank are examined.

2. Sampling and analysis

2.1. Samples studied

Our nationwide sampling program was based on the following: (1) the coal reserves of five main coal-bearing areas, (2) the production of 26 provinces in 2000, (3) coal rank and coal-forming period. In China, six coal-bearing areas can be identified, namely Permo-carboniferous (C-P) coal-bearing area in northern China, Late Permian (P₂) coal-bearing area in southern China, Early-Middle Jurassic (J₁₋₂) coal-bearing area in northwestern China, Late Jurassic (J₃) coal-bearing area in northeastern China, Mesozoic-Cenozoic (M-C) coal-bearing area in Yunnan Province and Tibet, and Tertiary (T) in Taiwan Province (Wang et al., 1992). The coal reserves in Yunnan Province and Tibet are less than 20 billion tons and exploitation is not yet well developed. Consequently only one coal sample was taken from this area. There are no coal mines in Shanghai and Tianjin Cities. The production of coals in Zhejiang Province, Hainan Province and Tibet is very low. Thus, there are no sampling sites in these regions. Coal sampling sites are shown in Fig. 1. The samples were collected from coal seam and the weight of every sample is about 5 kg. The samples were prepared by grinding, and screening through 200-mesh sieve. To avoid contamination and weathering, all samples were stored in plastic bags.

2.2. Reagents

Stock solution of 100 $\mu\text{g ml}^{-1}$ As was prepared by dissolving As₂O₃ 0.1320 g into the mixture of 2 ml 6 mol l⁻¹ NaOH and 50 ml de-ionized water. Then 2.5 ml 6 mol l⁻¹ H₂SO₄ was added into the solution, followed by being diluted to 1000 ml with de-ionized water. 50 ml of the stock solution was diluted to 500 ml to make standard solution.

KI solution was prepared by dissolving 3 g KI into 17 ml de-ionized water before being used.

SnCl₂ solution was prepared by dissolving 8 g SnCl₂ into 12 ml 36.5% HCl.

I₂ solution was prepared by dissolving 9 g KI and 1.5 g I₂ into de-ionized water and being diluted to 1000 ml.

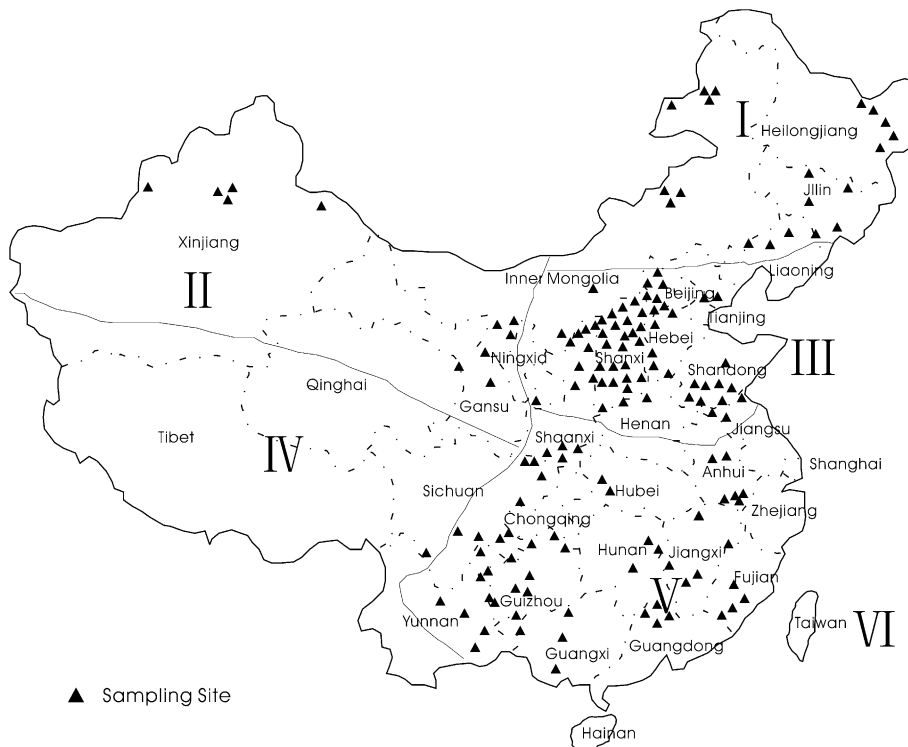


Fig. 1. Sketch map showing the sampling sites of coal in China (after Wu et al., 2004). I. C–P in northern China; II. P₂ in southern China; III. J₃ in northeastern China; IV. J_{1–2} in northwestern China V. M–C in Yuna and Tibet; VI. T in Taiwan province. 1 conical flask; 2 cotton; 3 tube; 4 zinc.

(NH₄)₆Mo₇O₂₄ solution was prepared by dissolving 10 g (NH₄)₆Mo₇O₂₄·4H₂O into 1000 ml 5 mol l⁻¹ H₂SO₄. (NH₂)₂·H₂SO₄ solution was prepared by dissolving 1.2 g (NH₂)₂·H₂SO₄ into 1000 ml de-ionized water. Same volumes of the two kinds of solution were mixed before being used.

Each zinc grain was the size of 5 mm and no arsenic contained.

NaHCO₃ solution was prepared by dissolving 40 g NaHCO₃ into 1000 ml de-ionized water.

Absorbent cotton was soaked by 400 g l⁻¹ Pb(AC)₂ solution and was dried at 80–100 °C.

2.3. Analytical procedures

A 1.000 g of finely ground coal sample and 2 g Eschka were finely mixed in a 30-ml graphite crucible and then covered with 1 g Eschka. The graphite crucible was heated at 800 ± 10 °C in muffle and was being kept at this temperature for about 2–3 h. After cooling, the mixture was transferred into a

conical flask by using 20 ml 6 mol l⁻¹ H₂SO₄ and 30 ml 6 mol l⁻¹ HCl. The solution was shaken after being added 2 ml KI solution and 1 ml SnCl₂ solution into the conical flask. At the same time 3 ml I₂ solution, 1 ml NaHCO₃ solution and 6 ml de-ionized water were added into the a tube. Then the conical flask and tube was connected with a glass tube that filled with absorbent cotton. After 15 min, 5 g Zinc grains were added into the conical flask. The reaction was maintained about 1 h. Add the mixture of

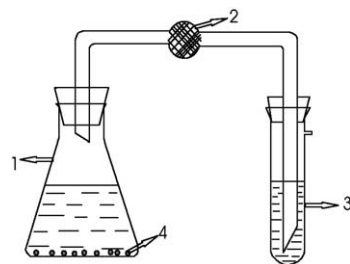


Fig. 2. The plot of the experiment.

Table 1
The reproducibility of experiment

The value of first testing	The value of second testing	Mean	RSD (%)
2.4	1.8	2.1	14.3
5.2	4.7	5.0	5.0
9.4	9.4	9.4	0
27.1	29.9	28.5	4.9
54.5	51.9	53.2	2.4

(NH₄)₆Mo₇O₂₄ solution and (NH₂)₂·H₂SO₄ solution 5 ml into the tube. The solution was being shaken and heated in boiling water for 20 min. After cooling, the solution was measured by spectrophotometer. The arsenic content of coal was performed with plotting calibration curve. The instrument is shown in Fig. 2.

GB11116 (34 mg/kg of arsenic content) is used as analytical calibration during experiment. The analytical precision, determined quality assurance, control procedures, using duplicates, blanks, was better than 15%. The detection limit of As is 0.09 mg ml⁻¹. The reproducibility of this method is shown in Table 1. This method is the Chinese standard method of Arsenic determination in coal and is widely used in China, so it is used in this study.

3. Result and discussion

3.1. Contents of Arsenic in coals of 26 provinces

The concentration distribution of arsenic in coals of twenty-six provinces of China is shown in Table 2. It shows that there are seven provinces whose average arsenic contents exceed 8 mg/kg, viz. Guangxi, Fujian, Inner Mongolia, Yunnan, Jilin, Jiangxi and Liaoning Provinces. Coals from these provinces should give rise to greater environmental concerns during combustion. It is necessary to point out that although arsenic contents of Guangxi and Fujian Province are very high, the numbers of samples are small, and further follow-up work needs to be carried out.

The results of arsenic concentrations in coals of five coal-bearing areas are listed in Table 3. The highest arsenic content (71 mg/kg) and the lowest arsenic content (0.2 mg/kg) were found in northern China. The mean arsenic contents were higher in

southern and northeast China, but lower in northwestern China.

3.2. The distribution of Arsenic contents in coals of different coal-forming periods and coal ranks

All coal samples are collected from ten coal-forming periods, namely, Early Carboniferous (C₁), Middle Carboniferous (C₂), Late Carboniferous (C₃), Early Permian (P₁), Late Permian (P₂), Late Triassic (T₃), Early Jurassic (J₁), Middle Jurassic (J₂), Late Jurassic (J₃), Tertiary (R) (Wu et al., 2004). The Table 4 shows that the highest arsenic concentration is 13 mg/kg and the lowest arsenic concentration is 4.2 mg/kg, respectively from R and P₁. From Fig. 3, the arsenic contents decreases in the order: R>J₁>T₃>J₃>J₂>P₂>C₁>C₂>C₃>P₁.

Table 2
The distribution of Arsenic contents in coals of 26 provinces (mg/kg)

Province	Range	Mean	Geometric mean	Standard deviation	Number of samples
Guangxi	7.7–50	24	19	18	5
Fujian	6.7–19	12	11	6.3	3
Inner Mongolia	1.0–53	10	5.5	13	17
Yunnan	2.1–27	10	5.9	11	7
Jilin	4.1–26	10	7.2	11	4
Jiangxi	2.8–24	9.3	7.2	7.4	7
Liaoning	0.61–29	8.1	4.9	8.7	9
Guizhou	0.52–45	7.5	4.6	10	17
Sichuan	0.66–21	6.7	4.2	6.6	8
Henna	0.36–71	6.2	2.3	15	23
Hunan	0.52–21	6.1	4.3	5.7	10
Shanxi	0.32–35	5.7	3.8	6.7	84
Shandong	1.4–27	5.7	3.9	6.6	20
Ningxia	3.1–9.9	5.7	5.2	2.9	4
Anhui	1.8–20	5.4	4.2	5.3	10
Hubei	1.3–7.9	5.2	4.0	3.5	3
Guangdong	4.6–5.5	5.1	5.0	0.62	2
Jiangsu	1.8–9.0	4.6	4.1	2.5	6
Hebei	1.3–9.6	4.3	3.6	2.6	15
Chongqing	0.66–8.6	4.3	3.2	2.9	8
Xinjiang	0.68–7.8	4.1	2.7	3.2	5
Shaanxi	0.24–15	3.8	2.2	4.2	12
Gansu	1.3–6.5	3.6	2.9	2.6	5
Qinghai	–	3.3	–	–	1
Heilongjiang	1.0–5.9	3.2	2.8	1.6	10
Beijing	–	2.9	–	–	1
Mainland	0.24–71	6.4	4.0	8.5	297

Table 3
Contents of Arsenic in coals of five coal-bearing areas (mg/kg)

Coal-bearing area	Range	Mean	Geometric mean	Standard deviation	Number of samples
C–P in northern China	0.24–71	5.4	3.4	0.56	184
P ₂ in southern China	0.52–50	8.5	5.34	1.1	70
J ₃ in northeastern China	0.61–53	8.8	5.0	2.1	31
J _{1–2} in northwestern China	0.68–7.8	4.2	3.2	0.75	11
M–C in Yuna and Tibet	–	3.4	–	–	1

Although there is a relationship between the concentrations of arsenic in coal and the coal ranks, the variation of arsenic contents in coal is not always correlated with the coal ranks (Chen, 2001). As shown in Table 5, Arsenic content decreases gradually from subbituminous through anthracite to bituminous.

It is clear that trace elements in coals have diverse origins. The concentrations of trace elements in coals are affected by many factors. Source material, depositional environment, climatic and hydrologic conditions are the controlling factors of trace elements during the early stages of coal formation. However, rank, tectonic setting and geochemical nature of groundwater and country rocks have greater influence during the coalification stages (Swaine and Goodarzi, 1995). Most of these factors are regional (Ren et al., 1999a,b; Ding et al., 2001). So it is difficult to found a relationship between arsenic contents of Chinese coals and coal-forming periods and coal ranks. Even though the relationship can be set up, it is most likely meaningless. Only the influential geological factors are excluded, will the relationship between arsenic content and coal-forming periods and coal rank rationalize. Therefore, such studies are more meaningful for one coal seam.

3.3. Arsenic contents in Chinese coal

The arsenic contents in Chinese coals range in this study from 0.2 to 71 mg/kg. Such values are not exceptionally high. There are 249 coal samples containing arsenic contents in the range of 0.24–8 mg/kg, accounting for 84% of all coal samples in this study. The contents of arsenic in Chinese coals exhibit a logarithmic normal frequency distribution (Fig. 4). Hence arsenic contents in Chinese coals show a geometric mean value of 4.0 ± 8.5 mg/kg. The mean of arsenic content in Chinese coals is 6.4 mg/kg. Weighed by the reserves of the five main coal-cumulating areas (Mao and Xu, 1999), it is 5.3 mg/kg, but weighed by the coal productions of 26 provinces in 2001, it is 6.0 mg/kg. Even though the reserves of high arsenic coals in Guizhou Province are considered, the result is still 6.0 mg/kg.

Table 6 shows that the average arsenic content of Chinese coals is obviously lower than that of Bohemia, America and the U.K., but higher than that of Australia and the average of the whole world. In order to avoid errors from too low and too high values, 90% of values are often adopted. An estimate of the most probable concentration can be calculated and be designated as the geometric mean (Swaine,

Table 4
The distribution of Arsenic contents in coals of different coal-forming periods (mg/kg)

Geological age	Range	Mean	Geometric mean	Standard deviation	Number of samples
Early Carboniferous (C ₁)	4.0–7.7	5.8	5.5	2.7	2
Middle Carboniferous (C ₂)	–	5.7	–	–	1
Late Carboniferous (C ₃)	0.24–32	5.4	3.8	5.4	57
Early Permian (P ₁)	0.32–27	4.2	3.1	4.1	85
Late Permian (P ₂)	0.52–50	6.5	4.0	9.1	58
Late Triassic (T ₃)	1.8–26	8.6	6.1	7.8	11
Early Jurassic (J ₁)	0.68–71	11	5.1	19	13
Middle Jurassic (J ₂)	0.52–34	6.9	4.1	8.2	34
Late Jurassic (J ₃)	0.61–53	8.6	4.6	12	22
Tertiary (R)	2.0–34	13	7.9	11	14

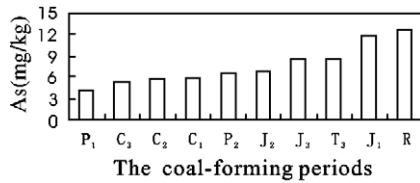


Fig. 3. The Arsenic contents in coals of different coal-forming periods.

1990). Table 6 shows that the average arsenic value in Chinese coals (6.4 mg/kg) is obviously lower than 276.6 mg/kg by Ren et al. (1999a,b). But the geometric means from both this study and Ren et al. (1999a,b) are similar. So the comparison with geometric mean is more meaningful. The geometric mean of arsenic in Chinese coals is close to that in American coals but far lowers than Bohemia coals. Although most of Chinese coals containing lower arsenic, the quantities of the medium and high arsenic containing coals are huge. Considering the fewer selection of raw coals in China, more and more low arsenic coals should be mined.

It is very interesting that arsenic contents in most coals of China are not high, but 3000 cases of arsenism are found in Guizhou Province, China (Zheng et al., 1999). Three reasons can be advanced to explain the endemic arsenic poisoning. Firstly, most of the coal in the Guizhou Province is high arsenic coal; it is used directly as fuel and never cleaned before burning. Secondly, the residents of this area traditionally use open coal-burning stoves. The arsenic is transferred into the ambient environment easily, e.g., air, dust, water, food. The arsenic content of indoor air of local residents was 8 times higher than state standard (An et al., 1995). Thirdly, open coal-burning stoves dry main foods such as the local peppers and crops. Unfortunately, peppers and crops will be enriched in arsenic greatly. For example, the arsenic contents in dried peppers and crops are up to 590 and 23 mg/kg,

Table 5
The distribution of Arsenic contents in coals of different coal rank (mg/kg)

Coal rank	Range	Mean	Geometric mean	Standard deviation	Number of samples
Subbituminous	0.61–53	11.6	6.3	13	25
Bituminous	0.24–71	5.7	3.8	7.2	208
Anthracite	0.36–50	6.9	3.9	9.5	64

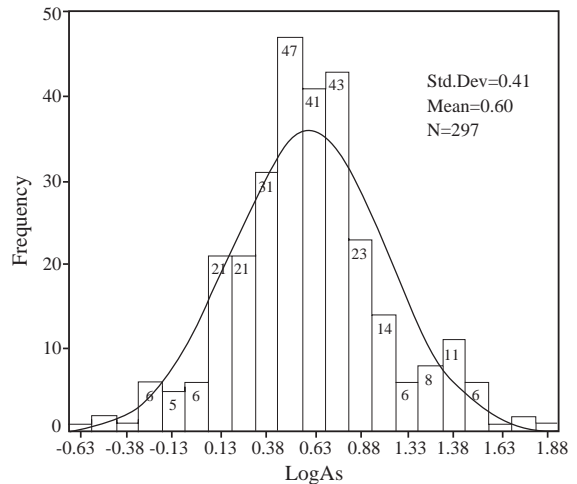


Fig. 4. Distribution of Arsenic contents in Chinese coals.

respectively which is 70 and almost 900 times higher than the fresh samples (An et al., 1995). Thus, the health of the local residents is severely impaired through ingestion of contaminated crops and peppers all the year round.

Similar way of indoor coal combustion, food drying and storing can be found in many regions in China. Up to now, only 3000 cases of arsenism were found in Guizhou Province, but it does not mean that the people in other regions are safe. The potential for significant health risks from coal-derived arsenism may exist elsewhere in China. The most effective measures to avoid arsenism are to change the life-style and habits of people in these regions and to switch from coal to wood for home heating. Only

Table 6
Contents of Arsenic in Chinese coal and the worldwide coals (mg/kg)

Arsenic	Range	Mean	Geometric mean	Number of samples
Chinese coal ^a	0.24–71	6.4	4.0	297
Chinese coal ^b	0.21–32000	276.6	4.2	132
American coal ^c	up to 2200	24	6.5	7676
U.K coal ^d	2–73	15		
Australian coal ^d	0.2–9	1.5		
Bohemian coal ^c		39.94	20.53	9172
World coal ^d	0.5–80	5.0 ^f		

^a This study; ^b Ren et al., 1999a,b; ^c Coal Quality Database; ^d Swaine, 1990; ^e Bouska and Pesex, 1994; ^f PECH, 1980.

when effective controls measures are applied will the risk caused by coal be reduced to the lowest.

4. Conclusion

Arsenic is a teratogen and a carcinogen. Arsenic in coal may pose high potential risks on humans and environment by combustion. For the environmental concern, knowing the concentration distribution of arsenic in Chinese coals is very important. In fact, it is quite difficult to obtain the proper distribution of arsenic contents in Chinese coals from limited coal samples. Thus, the establishment of proper planning is a significant factor. Moreover, it is important to conclude in a rational way. In this study, it is necessary to weigh the average value of the estimated reserves and the average value of annual production.

In comparison with worldwide coals, the level of arsenic in Chinese coal is not high. The reason for increased risk from arsenic in China is due to the arsenic-bearing coal smoke exposure in homes. Elimination of the exposure to coal-smoke exposure will effectively eliminate the problem.

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