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Fractionation and speciation of arsenic in fresh and combusted coal wastes from Yangquan, northern China

Xubo Gao · Yanxin Wang · Qinhong Hu

Abstract In this study, the content and speciation of arsenic in coal waste and gas condensates from coal waste fires were investigated, respectively, using the digestion and sequential extraction methods. The fresh and fired-coal waste samples were collected from Yangquan, which is one of the major coal production regions in northern China. High-performance liquid chromatography-inductively coupled plasma-mass spectrometry (HPLC-ICP-MS) was used to determine the concentrations of four major arsenic species [As(III), As(V), monomethylarsonic acid (MMA) and dimethylarsenic acid (DMA)] in the extracts, while ICP-MS was used to measure total As content. Arsenic content in the investigated coal wastes and the condensate ranges between 23.3 and 69.3 mg/kg, which are higher than its reported average content in soils. Arsenic in coal waste exists primarily in the residual fraction; this is followed in decreasing order by the organic matter-bound, Fe–Mn oxides-bound, exchangeable, carbonates-bound, and water-soluble fractions. The high content of arsenic in the condensates indicates that combustion or spontaneous combustion is one of the major ways for arsenic release into the environment from coal waste. About 15% of the arsenic in the condensate sample is labile and can release into the environment under leaching processes. The water extractable arsenic (WEA) in the fresh coal waste, fired coal wastes, and the condensate varied between 14.6 and 341 μg/kg, with As(V) as the major species. Furthermore, both MMA and DMA were found in fresh coal wastes, fired coal wastes, and the condensate.

Keywords Coal waste · Arsenic · Species · HPLC-ICP-MS · Environmental pollution

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Introduction

Arsenic (As) is a naturally occurring element; volcanic activity, rock weathering, and forest fires are the common natural mechanisms of arsenic release (Welch et al. 1988; Korte 1991; Mitchell and Barr 1995; Hindmarsh 2000; Smedley and Kinniburgh 2002). Arsenic is strongly chalcophile and can attain concentrations in the percentage range in sulfide ore assemblages, most commonly coexisting with pyrite (FeS_2) or in the form of arsenopyrite (FeAsS) and mono-metallic sulfides such as realgar (As_4S_4) (Waychunas et al. 1993; Nickson et al. 1998).

Over the past two decades, major efforts have been made to study the environmental geochemistry of geogenic arsenic (Nickson et al. 1998; Smedley and Kinniburgh 2002; Wang et al. 2009; Gao et al. 2011). Anthropogenic sources have become increasingly important in bringing As concentrations up to harmful levels in air, water, food, and forage (Blssen and Frimmel 2003; Yudovich and Ketris 2005; Romero et al. 2006; Roychowdhury et al. 2008).

For instance, it has been estimated that the total emission of arsenic from coal combustion in China was more than 1,500 tonnes in 2005 (Tian and Qu 2009). Systematic work is urgently needed to understand sources of anthropogenic arsenic in the environment, such as coal-mining activities, and to understand the fate of arsenic following environmental release. Oxidation of As-bearing ore and gangue minerals in mining activities has been highlighted as a cause of arsenic contamination of surface drainage and groundwater in several countries (Farag et al. 1998; Foster et al. 1998; Roussel et al. 2000; Bednar et al. 2002; Finkelman et al. 2002; Huggins et al. 2002). Fergusson (1990) noted that mining activities may cause arsenic concentrations in natural waters to increase locally from a background value in the 1–10 µg/L range to a range as high as 100–5,000 µg/L. Arsenic can also be emitted to the air via coal combustion (Polissar et al. 2001; Pavageau et al. 2002; Liu et al. 2002; Ng et al. 2003), since some coals and fly ash contain unusually high arsenic concentrations (Gentzis and Goodarzi 2000; Rodushkin et al. 2000).

The toxicity of arsenic varies widely among its different species (e.g., As(III), As(V), DMA, and MMA). As(III) is about 60 times more toxic than As(V), and inorganic arsenic species are more toxic than organoarsenicals (Thomas et al. 2001). Monomethylarsonic acid (MMA) and dimethylarsenic acid (DMA) are the two main organic As species that are somewhat toxic. However, as pointed out by Querol et al. (2008), little is known about the concentrations, occurrence, and speciation of arsenic in coal waste or in the leachate of coal waste banks containing high contents of iron and sulfur.

As the largest coal production country in the world, China has over 1,500 coal waste dumps, containing a total quantity of more than 5 gigatonnes (Gt) of waste. Moreover, the amount of coal gangue dumped into the environment has been increasing at a rate of 1.5–2.0 billion tons per year. In Shanxi Province, the total amount of coal waste is more than 1.3 Gt in 2007, occupying a land area of more than 0.2 million km^2.

Using samples from Yangquan city of Shanxi Province, one of the major coal-mining areas in northern China, this paper reports on investigations of the occurrence and speciation of arsenic in coal wastes using high-performance liquid chromatography-inductively coupled plasma-mass spectrometry (HPLC-ICP-MS).

Materials and methods

Sample preparation

Four coal waste samples and one condensate sample were collected from the coal waste banks of Yangquan, one of the largest Coal Industrial Groups of the Qingshui coalfields in Shanxi Province. The two major periods of coal formation in the Yangquan area include the Carboniferous (Taiyuan Formation) and the Early Permian (Shanxi Formation). The lithology of the Taiyuan Formation consists mainly of quartz sandstone, siltstone, silty mudstone, mudstone, limestone, and coal. The lithology of the Shanxi Formation is composed mainly of arkose, siltstone, silty mudstone, mudstone, and coal. The samples used in this work were collected from an exposure of coal waste gobs deposited less than 2 years ago. Samples were collected around, and also the top of, the coal waste banks; about one kilogram material was collected for each sample. Because the shape of coal waste bank is a half-circle, samples were collected every 50 m around the top and along the foot front. After collection, samples were sorted in the lab according to their lithology. The determination of lithology was performed using two methods: the major minerals method and the burning method, in which samples were burnt in a muffle furnace at 700–900°C till the black color disappeared, and then identified by eye and microscope observations. To study As speciation in different types of coal wastes, four samples of different source-rock composition were selected: one from limestone (EHG), one from shale (YIG), and two from sandstone (EAG and YJG). The condensate sample was collected from a spontaneously combusted coal gangue bank where it

was covered with loess and sandy soil; the condensate sample was separated from the cover materials by a knife. All collected samples were stored in plastic bags after being wrapped with aluminum foil to prevent contamination.

To determine water extractable arsenic and arsenic species in fired coal waste, about 100 g of the above four coal waste samples (EHG, YIG, EAG, and YJG) were heated at $1,100 \pm 30^\circ C$ to approximate conditions expected in the coal fire (as suggested by Querol et al. 2008) in a muffle furnace (Thermolyne 48000) for 1 h, after a heating increase rate of about $20^\circ C/min$; the remains were labeled as fired-coal waste samples EHGF, YIGF, EAGF, and YJGF, respectively.

All the samples (coal waste, fired coal waste, and the condensate) were pulverized and sieved through 150 mesh size. The homogenized samples were air dried and then stored in desiccators before use.

Extractions using DI water were conducted to investigate water-extractable arsenic speciation in the coal wastes, in the fired coal wastes, in the condensate sample, and in samples of NIST standard reference soils (Montana soils 2710 and 2711). Extraction of arsenic was performed by adding 4 mL deionized water to approximately 1 g of solid sample. The mixture was shaken for 24 h on a table shaker and centrifuged at 6,000 rpm for 30 min to remove particle sizes larger than 0.45 μm; it was then filtrated through a 0.2-μm membrane filter (Pall Life Sciences). The filtrate was analyzed using a coupled LC-ICP-MS.

Sample digestion for total arsenic determination followed EPA method 3050B, with high-purity nitric acid (HNO_3) and hydrogen peroxide (H_2O_2) repeatedly added to 0.1 g (dry weight) of sample for digestion. For consequent ICP-MS analyses, the resultant digestate was reduced in volume by heating ($95^\circ C$) and was then diluted to a final volume of 50 mL in 1% HNO_3.

A sequential extraction experiment was performed based on the methods suggested by Tessier et al. (1979) to study the occurrence of arsenic in the coal waste and in the condensate samples. The following list describes the procedures or steps; the arsenic fraction targeted by each step is indicated in parentheses. In steps 1 through 5, a solid/solution ratio of 1:25 was employed.

Step 1 (for water-soluble fraction): 50 mL of deionized H_2O at room temperature (about $23^\circ C$)

was added to the solid material, and contact (roll shake shaking in low speed) was maintained for 1 h;

Step 2 (for exchangeable fraction): a solution of 1 M $MgCl_2$, at a pH of 7.0 and at room temperature, was added to the sample, maintaining contact for 1 h;

Step 3 (for the fraction bound to carbonates or specifically adsorbed): one mole of NaOAc solution at a pH of 5.0, buffered with HOAc and at room temperature, was added to the sample, maintaining contact for a period of 5 h;

Step 4 (for the fraction bound to Fe–Mn oxides): 0.04 mol of $NH_2OH \cdot HCl$ in 25% HOAc (pH 2.0, $96^\circ C$ in a water bath) was added to the sample, maintaining contact for a period of 5 h;

Step 5 (for the fraction bound to organic matter): 50 mL of 3.2 M NH_4Ac after the mixture of 20 mL of 0.02 M HNO_3 (pH 2.0) and 30 mL of 30% H_2O_2 was added and heated to $85^\circ C$ (in a water bath) for 2 h;

Step 6 (for residue fraction): calculated by the difference between the total arsenic content in coal waste samples, measured from total digestion, and the combined arsenic amounts from Steps 1 to 5.

Reagents

Sodium meta-arsenite ($NaAsO_2$) and DMA were purchased from Mallinckrodt Baker, Inc (Phillipsburg, NJ). Sodium hydrogen arsenate heptahydrate ($Na_2HAsO_4 \cdot 7H_2O$) and MMA were obtained from Alfa Aesar Company (Ward Hill, MA) and Sigma–Aldrich (St. Louis, MO), respectively. Reagents used for the HPLC mobile phases included ammonium phosphate dibasic (supplied by Acros organics, Fair Lawn, NJ), Aristar Ultra nitric acid (VWR International, West Chester, PA), and high-purity ammonium hydroxide (VWR International). Ultrapure water for analysis was prepared using a water purification system (Element A10 and Elix 10, Millipore, Billerica, MA).

The reference Montana soil 2711 (with a reported value of 105 ± 8 mg of As kg^{-1}) and soil 2710 (626 ± 38 mg of As kg^{-1}) were obtained from the National Institute of Standards and Technology (Gaithersburg, MD). Certified reference liquid materials TM-26.3 and TMDA-54.4 (total As at 7.9 and

43.6 μg/L, respectively) supplied by the National Laboratory for Environmental Testing, Environment Canada was used to validate the LC-ICP-MS analytical procedure.

Analytical conditions for HPLC- and ICP-MS

Arsenic speciation analysis was performed using two instrumental systems, HPLC and ICP-MS. The HPLC system consists of a quaternary pump and an autosampler (Series 200, PerkinElmer, Waltham, MA). Operating parameters of the isocratic separation of As species was as follows: mobile phase, 10 mM ammonium nitrate and 10 mM ammonium phosphate at pH 9.4 (adjusted with ammonium hydroxide); flow rate, 1.5 mL/min; sample injection volume, 100 μL. The separation was achieved on a Hamilton PRP-X100 (Sparks, NV) anion-exchange column (4.1 × 250 mm, 10 μm) and a guard column. The HPLC column outlet was directly connected, via 60 cm of trifluoroacetic acid capillary tubing (1.6 mm o.d. × 0.5 mm i.d.), to the nebulizer of ICP-MS.

A PerkinElmer SCIEX model Elan® DRC II ICP-MS was used for arsenic measurements. The instrument conditions for ICP-MS were as follows: RF power, 1,300 W; plasma argon gas flow 15 L/min; nebulizer argon gas flow 0.9 L/min; auxiliary argon gas flow 1.2 L/min; Meinhard Type A quartz nebulizer; platinum sampling; and skimmer cones. For the determination of total arsenic content, a standard solution with 5 ppb of In-115, Sc-45, Li-6, and Bi-209 was used as internal standard for ICP-MS measurement.

Stock standard solutions of As(III), As(V), MMA, and DMA were prepared by dissolving each chemical compound in autoclaved ultrapure water at a concentration of 100 mg/L (arsenic content) in a separate autoclaved amber glass bottle. Each individual As species was prepared to obtain the retention time from HPLC separation for peak identification. However, working standard solutions, in the range of 0.001–1 mg/L As, were prepared by diluting the stock standard solution of DMA only (Sun et al. 2008). ICP-MS detection mass was set at m/z 75 ($^{75}As^{+}$). The accuracy of the analyses was confirmed using reference material TMDA-54.4, which has reported values for As(III) and As(V).

Results and discussion

Total arsenic content

The minerals of the coal gangue samples are mainly quartz (44–67%), calcite (6–43%), and kaolinite (5–10%), with a minor proportion of pyrite (0.7–1.8%). The mineral assemblage of the fired coal gangue contains quartz, mullite, mascagnine, syngenite, lazurite, and anhydrite. The X-ray diffraction detectable compounds in the condensate sample are elemental sulfur and koktaite that are sublimates from gaseous emissions. Table 1 reports the total arsenic content in the investigated coal wastes and condensates, common values in soil, and the average abundance in the Earth's crust (Alloway 1990). The elemental concentrations of coal samples fell within or above the reported values in soil. The highest

Table 1 Contents of arsenic and other elements in the coal waste and the condensate sample, their reported values in soils and average abundance in the Earth's crust (mg/kg except pH, S, C, and ash content)

Sample ID\element	pH[a]	As	Fe	Mn	Ni	Cr	S (%)	C (%)	Ash content (%)
EHG	8.13	24.3	9,405	23.7	39.6	265	0.32	8.58	85.7
EAG	5.13	23.3	180,185	3,119	72.3	345	0.75	9.93	84.3
YIG	6.35	28.0	36,992	340	124	218	0.78	12.7	82.4
YJG	2.99	69.3	228,757	2,255	309	675	0.91	15.2	79.2
Condensate	3.07	23.5	3,521	19.1	300	292	–	–	–
Soils (Alloway 1990)	–	1–20	–	1,000	50	70–100	–	–	–
Average content in the Earth's crust (Alloway 1990)	–	40.0	50,000	1,000	80.0	200	–	–	–

[a] pH was measured with a solid: DI water ratio 1:4

arsenic content was found in the coal waste sample YJG (sandstone, 69.3 mg/kg), followed by YIG (sandstone, 28.0 mg/kg), EHG (limestone, 24.3 mg/kg), and EAG (shale, 23.3 mg/kg). The highest content of iron (228,757 mg/kg), as well as the second-highest content of manganese (2,255 mg/kg), was found in the sandstone sample YJG. The arsenic content in the limestone sample (EHG) is almost the same as YIG and EAG samples, though the contents of iron and manganese in EHG (9,405 and 23.7 mg/kg, respectively) are far lower than that in the shale (180,185 and 3,199 mg/kg, respectively) and sandstone (132,875 and 1,298 mg/kg, respectively). This indicates that the arsenic content in coal waste is not always positively related to the Fe–Mn contents in coal gangue samples. The total sulfur percentage in coal waste samples YJG, YIG, EAG, and EHG is very small to be 0.91, 0.78, 0.75, and 0.32, respectively. The percentage of pyritic sulfur in total sulfur is about 75.0, 68.0, 62.0, and 53.0, respectively, which indicates that pyrite is one of the major forms of small sulfur presence in coal wastes.

Arsenic content in the condensates is almost at the same level as in the three coal waste samples (EHG, EAG, and YIG) and shows a low content of iron (3,521 mg/kg) and manganese (19.1 mg/kg). In summary, these results show that coal waste is a significant source of arsenic in the environment, with a measured As concentration from 23.3 to 69.3 in Yangquan samples.

The coal in the study area has low moisture content (1.5%), low to high S (0.3–4.4%), and high-ash (33%). The C content is 82.1%, and the calorific value reaches 32.1 MJ/kg. The N, H, and O contents are 1.4, 3.7, and 2.7%, respectively. The arsenic content in the coal ranges from below-the-detection-limit to 82.4 mg/kg.

Sequential extraction

Leaching is one major way for arsenic release from coal waste banks, especially in view of their long-term dumping. Sequential extraction provides a means of studying the potential mobility of arsenic in coal waste and in the condensate materials and can provide insights regarding mechanisms of secondary pollution of arsenic in the condensates. For these reasons, a sequential extraction experiment was performed on the four coal waste samples and on

the condensate sample. Though arsenic coexisting with sulfide is the major form in the coal waste, a six-step heavy metal extraction method suggested by Tessier et al. (1979) was used here to make it comparable with many other reports of heavy metals in various geological samples. There are some recent extraction methods reported for coal samples (Norris et al. 2010; Liu et al. 2011) that consider the importance of sulfides in the arsenic content, but these methods were not used in this study because of the low concentration of sulfides observed in our coal samples. The percentage of arsenic determined in each step of the sequential extraction is listed in Table 2.

The percentage of water-soluble arsenic fraction (Step 1) in coal gangue is low, ranging from 0.05 to 0.29%, with an average value of 0.14% (Table 2). Given the relatively short periods of water–mineral reaction time in the experiment, arsenic in this fraction is assumed to have been released from freely soluble components. The low percentages determined in this step suggest the absence of soluble arsenic minerals in coal waste. The pH value of the extracted solution for EHG, EAG, YIG, YJG, and the condensate is 7.32, 6.47, 6.89, 5.88, and 4.23, respectively. In Step 2, 1 M $MgCl_2$, a weak extractant, was used to extract metals weakly bound to the matrix (exchangeable fraction). Given the neutral characteristics of the applied extraction solution, specifically adsorbed trace elements would not be expected to have been desorbed completely. The percentages of arsenic extracted from the coal gangue samples in this step

Table 2 Percentage of arsenic extracted from each sequential extraction step

Sample ID	EHG	EAG	YIG	YJG	Condensate	Avg.
Fraction 1	0.11	0.11	0.29	0.05	1.25	0.14
Fraction 2	2.81	3.34	3.98	1.68	4.45	2.95
Fraction 3	0.58	3.84	3.05	1.42	5.53	2.22
Fraction 4	2.54	4.68	2.02	8.49	2.38	4.43
Fraction 5	15.9	4.92	6.89	13.1	1.25	10.2
Fraction 6	78.1	83.1	83.8	75.3	85.1	80.1

Fractions 1–6 is, respectively, the water-soluble fraction, exchangeable fraction, fraction bound to carbonates or specifically adsorbed, bound to Fe–Mn oxides, bound to organic matter, and the fraction in the residue; the percentage of fraction 6 is obtained by subtracting the total arsenic content from the sum of the other five fractions; Avg. is the average value for the four coal waste samples

were found to be modestly high, ranging between 1.68 and 3.98%. The extractant solution of the coal gangue samples from Step 2 is acidic to slightly alkaline, as indicated by the final pH values from 5.2–6.4 to 8.2 of the extraction solutions.

The extraction solution used in Step 3 is weakly acidic and expected to extract most of the arsenic bound to calcite, but not that associated with dolomite. However, due to the weak acidity (or alkalinity) of the final extraction solution in Step 2, the arsenic content extracted in Step 3 could be lower than the case if Step 2 was not employed before Step 3. The solution of 0.04 M $NH_2OH \cdot HCl$ in 25% HOAc used in Step 4 is a strong reductant, which can easily cause the decomposition of amorphous and slightly crystalline iron oxides. Therefore, the arsenic present in the Step 4 extraction solution predominantly comes from the dissolution of amorphous iron oxides and pyrolusite; the contribution of other natural manganese minerals, if present, at this step is very low, as suggested by Shan and Chen (1993). The arsenic content in fraction 4 obtained from the experiment may be a little lower than the real content of arsenic associated with iron or manganese oxides in the samples, because of the re-adsorption and redistribution of iron and manganese in solution. Shan and Chen (1993) reported that iron and manganese can either be re-adsorbed onto the surfaces of other phases or onto the surfaces of humic acids and clay minerals.

The extraction agent for Step 5 is an oxidant, with a mixture of hydrogen peroxide and nitric acid used as an extractant for the As fraction bound to organics. The medium–high value of arsenic percentages in fraction 5 indicates that the organic-bound arsenic is one of the major occurrences in coal gangue. The values for fraction 6 were obtained by subtracting the total arsenic percentage of 100%, from the other five fractions. Our results with Yangquan coal waste samples indicate that most of arsenic (>75%) was associated with recalcitrant phases in the coal gangue in the residual form (Table 2).

The order of arsenic occurrence in coal gangue (in terms of average percentage) is as follows: residue fraction (80.1%), bound to organic matter (10.2%), bound to Fe–Mn oxides (4.43%), exchangeable (2.95%), bound to carbonates or specifically adsorbed (2.22%), and the water-soluble fraction (0.14%). For the condensate sample, in contrast to the coal gangue

samples, the total arsenic extraction percentages for Steps 1 (1.25%), 2 (4.45%), and 3 (5.53%) were higher than the total for Steps 4 (2.38%) and 5 (1.25%), although the highest percentage was again found in Step 6 (85.1%). The results indicate that about 15% of the arsenic in the condensate sample is labile and prone to release into the environment.

Arsenic species

Based on the above results of sequential extraction experiments, leaching of arsenic from coal waste can have serious environmental effects. The distribution of arsenic species in natural solutions is of great significance due to the differences in toxicity of various species. The results of this study pertaining to the water extractable arsenic (WEA) and arsenic species of coal waste, fired coal waste, the condensate, and NIST reference soils are therefore of particular interest. The mean WEA in reference Montana soils 2710 and 2711 was $1,876 \pm 2.0$ and 164 ± 0.8 µg/kg ($n = 3$, dry mass), respectively (Table 3). The arsenic species in the WEA of reference Montana soil 2710 were found to be As(III) 38.8 µg/kg, DMA 12.2 µg/kg, MMA below the detection limit (calculated based on a liquid detection limit of 0.02 µg/L), and As(V) 1,830 µg/kg. For Montana soil 2711, the As species were determined as As(III) 41.4 µg/kg, DMA 18.0 µg/kg, MMA below detection limit, and As(V) 105 µg/kg. Measured WEA in the fresh coal waste varied between 33.9 and 95.9 µg/kg (dry mass) with an average value of 61.0 µg/kg, which is higher than the content of water-soluble arsenic in sequential extraction experiments. After 24-h shaking, solute in the slurry included not only the water-soluble fraction but also parts of the exchangeable fraction, the fraction bound to carbonates or specifically adsorbed, the fraction bound to Fe–Mn oxides, and the fraction bound to organic matter. Therefore, it is reasonable to have a WEA value higher than the water-soluble arsenic content in sequential extraction experiment. The highest WEA was found in the sample YIG (shale), in which the dominant species was As (V) at 79.2 µg/kg, followed by DMA (17.5 µg/kg), as shown in Table 3. The lowest WEA was found in the sample EAG, with DMA at 23.3 µg/kg as the dominant species, followed by 10.1 µg/kg of As(V) and 1.0 µg/kg of MMA (Figs. 1, 2, 3, 4).

Table 3 Water extractable arsenic (WEA) and arsenic species in selected samples and reference materials (µg/kg)

Sample ID	As(III)		DMA		MMA		As(V)		WEA (Calculated)	WEA (Measured)
	Content	Weight percent	Content	Weight percent	Content	Weight percent	Content	Weight percent		
Fresh coal waste										
EHG			17.5	48.2			18.8	51.8	36.2	36.8
EAG			23.3	67.7	1.0	2.9	10.1	29.4	34.4	33.9
YIG			17.5	18.1			79.2	81.9	96.7	95.9
YJG	28.6	36.9	16.5	21.3			32.4	41.8	77.6	77.3
Mean	28.6		18.7		1.0		35.1			61.0
Fired coal waste										
EHGF			13.0	45.6			15.5	54.4	28.5	29.0
EAGF			15.0	13.2			98.1	86.8	113	114
YIGF							14.9	100	14.9	14.6
YJGF	12.8	48.6					13.5	51.4	26.3	26.7
Mean	12.8	24.8	14.0	27.1			35.5	68.9	51.5	46.0
Condensate	32.6	9.49	25.4	7.39	146	42.4	140	40.8	344	341
Reference material										
TMDA-54.4	28.0	62.8					16.6	37.2	44.6	43.1
Montana soil 2710	38.8	2.06	12.2	0.65			1,830	97.3	1,881	1,876
Montana soil 2711	41.4	25.2	18.0	10.9			105	63.9	164	164

The unit of weight percent is %; WEA (calculated): summation of each arsenic species concentration from HPLC-ICP-MS; WEA (measured): total arsenic concentration measured by ICP-MS

Fig. 1 Chromatogram of HPLC-ICP-MS analyses for a standard solution of four arsenic species at 4 µg/L concentration for each species. *CPS* counts per second. The retention times of As(III), DMA, MMA, and As(V) is 1.80, 2.18, 3.50, and 5.55 min, respectively
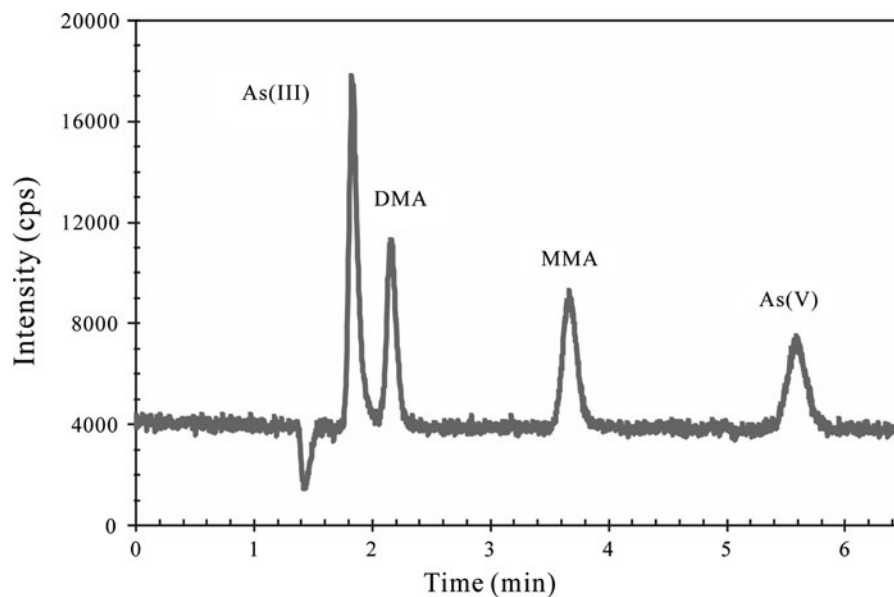
After heat-treatment of the fresh coal waste, most of the fired coal wastes had a lower WEA than the original coal waste samples, except for sample EAGF (sandstone, red color). It is well known that arsenic can enter the environment during coal burning, and so the reduction of WEA in fired coal gangue may result

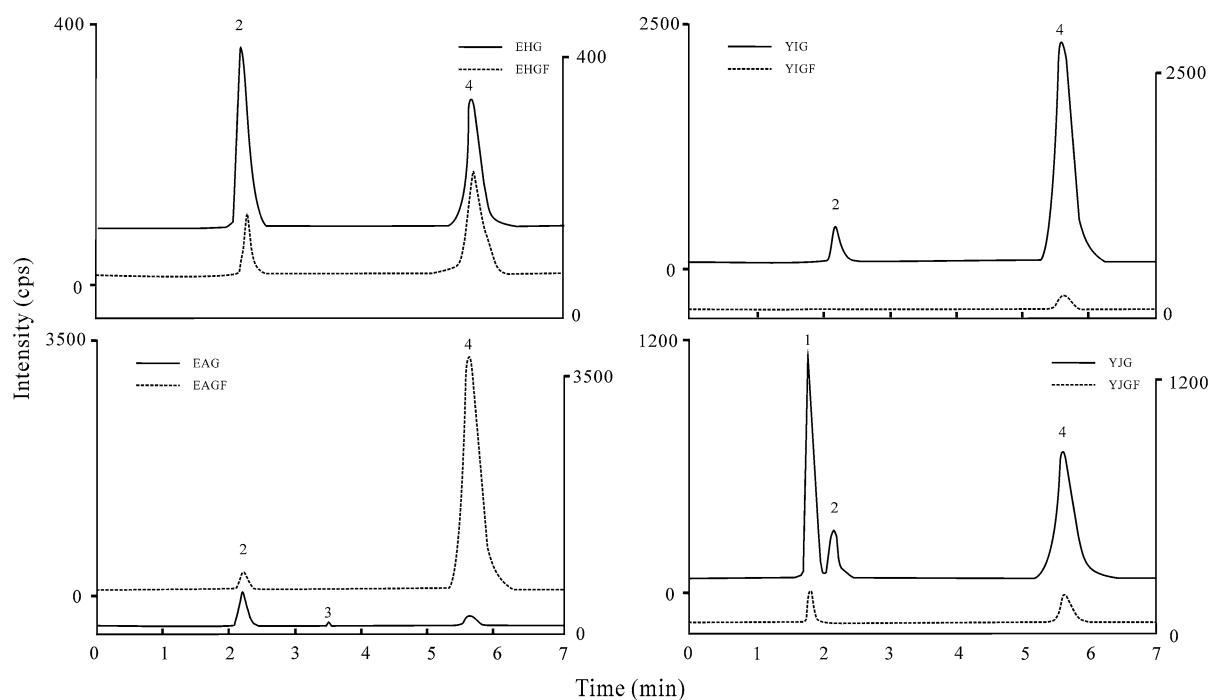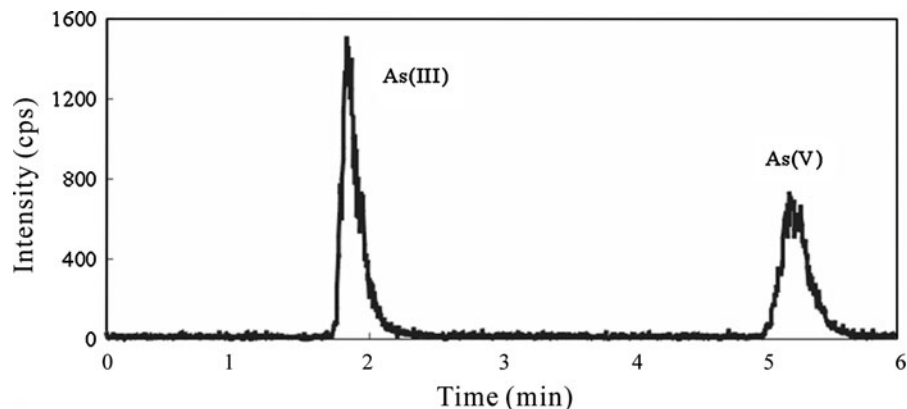**Fig. 2** Chromatogram of reference material TMDA-54.4

Fig. 3 Chromatograms of water extractable arsenic of the coal waste and fired-coal waste samples, solid liquid ratio 1:4. Arsenic species: 1-As(III), 2-DMA, 3-MMA, 4-As(V); The *y*-axis has the scale for intensity of YJGF, EHGF, EAGF, and YIGF

from more arsenic release. Furthermore, the WEA in the condensate, which is actually condensed gas material of spontaneous combustion of coal waste, was as high as 341 µg/kg, giving further evidence of the release of arsenic during coal waste combustion.

All of the four arsenic species were detected in the coal waste, fired coal waste, and the condensate. The highest MMA was detected in the condensate; little of this species was found in EAG, indicating that

MMA may be transformed from other species of arsenic during spontaneous combustion in coal waste banks. DMA was detected in all fresh coal wastes, in two of the fired coal waste samples and in the condensate. The DMA content in the coal waste sample was higher than that in the fired coal waste. The highest content of DMA was found in the coal waste sample EAG (23.3 µg/kg), suggesting that DMA can be an important arsenic species in coal waste, and that it can be transformed into other
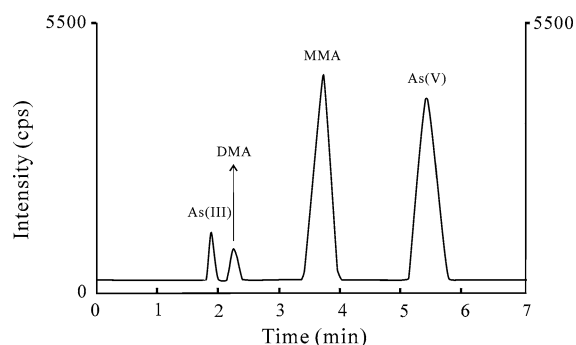
Fig. 4 Chromatogram of water extractable arsenic of the condensate sample, solid liquid ratio 1:4

arsenic species during high-temperature heating (1,100°C for 1 h in this work).

As(III) was found only in coal waste sample YJG and in its corresponding fired sample YJGF. As(V) is found to be the major As species in Yangquan coal waste samples. The concentrations of water extractable As(V) in the fresh coal waste ranged between 10.1 and 79.2 μg/kg (dry mass); that in the fired coal waste ranged between 13.5 and 98.1 μg/kg; and that in the condensate was 140 μg/kg. The water extractable As(V) in the fresh coal waste was higher than that in the corresponding fired-coal waste samples except for EAG. Compared to fresh coal waste, the declines in As(III), As(V), and DMA contents in most of the fired-coal waste samples further suggests As release and species transformation under heating conditions such as spontaneous combustion.

Conclusions

In terms of weight percent, arsenic contents in the investigated coal wastes and in the condensates were all above the reported average arsenic abundance in the Earth's crust (40.0 mg/kg, Alloway 1990). The order of arsenic content in the coal waste sample was YJG (sandstone, 69.3 mg/kg), YIG (sandstone, 28.0 mg/kg), EHG (limestone, 24.3 mg/kg), and EAG (shale, 23.3 mg/kg). According to our sequential extraction results, the content of arsenic in different fractions of coal waste decreased as follows: residual fraction (80.1%) > fraction bound to organic matter (10.2%) > fraction bound to Fe–Mn oxides (4.43%) > exchangeable fraction (2.95%) > fraction bound to carbonates or specifically adsorbed (2.22%) > water-

soluble fraction (0.14%). The high content of arsenic in the condensates suggests that combustion, such as spontaneous combustion of coal gangue banks, is one of the major ways for arsenic release into the environment from coal waste. For the condensate sample, about 15% of the arsenic is labile and can be released into the environment under leaching conditions.

The use of high-performance liquid chromatography-inductively coupled plasma-mass spectrometer proves to be a powerful tool for investigating arsenic speciation in coal waste extracts. Our results show that in the case of fresh coal waste, fired coal wastes, and the condensate, water extractable total arsenic exists mainly as As(V). Organic arsenic compounds were found in fresh coal waste, fired coal waste, and the condensate. Compared to fresh coal wastes, the elevation of WEA content in the condensates and its decrease in fired coal waste indicate that transformation of different arsenic species may occur during spontaneous combustion and leaching of coal waste banks. More attention should be paid to focus on the possible consequences of arsenic environmental toxicity from the above processes.

References

Alloway, B. J. (1990). *Heavy metals in soils*. John Wiley and Sons, Inc: New York.

Bednar, A. J., Garbarino, J. R., Ranville, J. F., & Wildeman, T. R. (2002). Preserving the distribution of inorganic arsenic species in groundwater and acid mine drainage samples. *Environmental Science and Technology, 36*(10), 2213–2218.

Blssen, M., & Frimmel, F. H. (2003). Arsenic: a review. Part I: Occurrence, toxicity, speciation, mobility. *Acta hydrochimica et hydrobiologica, 31*, 9–18.

Farag, A. M., Woodward, D. F., Goldstein, J. N., Brumbaugh, W. G., & Meyer, J. S. (1998). Concentrations of metals associated with mining waste in sediments, biofilm, benthic macro-invertebrates, and fish from the Coeur d'Alene River Basin, Idaho. *Archives of Environmental Contamination and Toxicology, 34*(2), 119–127.

Fergusson, J. E. (1990). *The heavy elements: Chemistry, environmental impact and health effects*. Oxford: Pergamon.

Finkelman, R. B., Orem, W., Castranova, V., Tatu, C. A., Belkin, H. E., Zheng, B. S., et al. (2002). Health impacts

of coal and coal use: Possible solutions. *International Journal of Coal Geology, 50*(1–4), 425–443.

Foster, A. L., Brown, G. E., Tingle, T. N., & Parks, G. A. (1998). Quantitative arsenic speciation in mine tailings using X-ray absorption spectroscopy. *American Mineralogist, 83*(5–6), 553–568.

Gao, X. B., Wang, Y. X., Hu, Q. H., & Su, C. L. (2011). Effects of anion competitive adsorption on arsenic enrichment in groundwater. *Journal of Environmental Science and Health Part A, 46*(5), 1–9.

Gentzis, T., & Goodarzi, F. (2000). Effect of geological processes on coal quality and utilization potential: Review with examples from western Canada. *Journal of Hazardous Materials, 74*(1–2), 109–124.

Hindmarsh, J. T. (2000). Arsenic, its clinical and environmental significance. *Journal of Trace Elements in Experimental Medicine, 13*(1), 165–172.

Huggins, F. E., Huffman, G. P., Kolker, A., Palmer, S. J., Mroczkowski, C. A., & Finkelman, R. B. (2002). Combined application of XAFS spectroscopy and sequential leaching for determination of arsenic speciation in coal. *Energy & Fuels, 16*, 1167–1172.

Korte, N. (1991). Naturally - occurring Arsenic in groundwaters of the mid western United State. *Environmental Geology and Water Sciences, 18*(2), 137–141.

Liu, H. Y., Yu, D., Yang, W., & Feng, L. (2011). The effect of mercury occurrence on mercury rejection during coal preparation. *International Journal of Coal Preparation and Utilization, 31*(1), 20–31.

Liu, J., Zheng, B., Vasken, A. H., Zhou, Y., Chen, M. L., Zhang, A., et al. (2002). Chronic arsenic poisoning from burning high-arsenic-containing coal in Guizhou, China. *Environmental Health Perspectives, 110*(2), 119–122.

Mitchell, P., & Barr, D. (1995). The nature and significance of public exposure to arsenic - A review of its relevance to south-west England. *Environmental Geochemistry and Health, 17*(2), 57–82.

Ng, J. C., Wang, J. P., & Shraim, A. (2003). A global health problem caused by arsenic from natural sources. *Chemosphere, 52*(9), 1353–1359.

Nickson, R., McArthur, J., Burgess, W., Ahmed, K. M., Ravenscroft, P., & Rahman, M. (1998). Arsenic poisoning of Bangladesh groundwater. *Nature, 395*(6700), 338.

Norris, P., Chen, C. W., & Pan, W. P. (2010). A technique for sequential leaching of coal and fly ash resulting in good recovery of trace elements. *Analytica Chimica Acta, 663*(1), 39–42.

Pavageau, M. P., Pecheyran, C., Krupp, E. M., Morin, A., & Donard, O. F. (2002). Volatile metal species in coal combustion flue gas. *Environmental Science and Technology, 36*(7), 1561–1573.

Polissar, A. V., Hopke, P. K., & Poirot, R. L. (2001). Atmospheric aerosol over Vermont: Chemical composition and sources. *Environmental Science and Technology, 35*(23), 4604–4621.

Querol, X., Izquierdo, M., Monfort, E., Alvarez, E., Font, O., Moreno, T., et al. (2008). Environmental characterization of burnt coal gangue banks at Yangquan, Shanxi Province, China. *International Journal of Coal Geology, 75*(2), 93–104.

Rodushkin, I., Axelsson, M. D., & Burman, E. (2000). Multi-element analysis of coal by ICP techniques using solution nebulization and laser ablation. *Talanta, 51*(4), 743–759.

Romero, F. M., Armienta, M. A., Villasenor, G., & Gonzalez, J. L. (2006). Mineralogical constraints on the mobility of arsenic in tailings from Zimapan, Hidalgo, Mexico. *International Journal of Environment and Pollution, 26*(1–3), 23–40.

Roussel, C., Bril, H., & Fernandez, A. (2000). Arsenic speciation: Involvement in evaluation of environmental impact caused by mine wastes. *Journal of Environmental Quality, 9*(1), 182–188.

Roychowdhury, T., Uchino, T., & Tokunaga, H. (2008). Effect of arsenic on soil, plant and foodstuffs by using irrigated groundwater and pond water from Nadia district, West Bengal. *International Journal of Environment and Pollution, 33*(2–3), 218–234.

Shan, X., & Chen, B. (1993). Evaluation of sequential extraction for speciation of trace mentals in model soil containing natural minerals and humic acid. *Analytical Chemistry, 65*(6), 802–807.

Smedley, P. L., & Kinniburgh, D. G. (2002). A review of the source, behaviour and distribution of arsenic in natural waters. *Applied Geochemistry, 17*(5), 517–568.

Sun, G.-X., Williams, P. N., Carey, A.-M., Zhu, Y.-G., Deacon, C., Raab, A., et al. (2008). Inorganic arsenic in rice bran and its products are an order of magnitude higher than in bulk grain. *Environmental Science and Technology, 42*(19), 7542–7546.

Tessier, A., Cambell, P. G. C., & Bisson, M. (1979). Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry, 51*, 844–851.

Thomas, D. J., Styblo, M., & Lin, S. (2001). The cellular metabolism and systemic toxicity of arsenic. *Toxicology and Applied Pharmacology, 176*(2), 127–144.

Tian, H. Z., & Qu, Y. P. (2009). Inventories of atmospheric arsenic emissions from coal combustion in China, 2005. *Environmental Science, 30*(4), 956–962. (in Chinese with English abstract).

Wang, Y. X., Shvartsev, S. L., & Su, C. L. (2009). Genesis of arsenic/fluoride-enriched soda water: A case study at Datong, northern China. *Applied Geochemistry, 24*(4), 641–649.

Waychunas, G. A., Rea, B. A., Fuller, C. C., & Davis, J. A. (1993). Surface-chemistry of ferrihydrite. 1. EXAFS studies of the geometry of coprecipitated and adsorbed arsenate. *Geochimica et Cosmochimica Acta, 57*(10), 2251–2269.

Welch, A. H., Lico, M. S., & Hughes, J. L. (1988). Arsenic in groundwater of the western United States. *Ground Water, 26*(3), 333–347.

Yudovich, Ya. E., & Ketris, M. P. (2005). Arsenic in coal: A review. *International Journal of Coal Geology, 61*, 141–196.