

# Fractions and leaching characteristics of mercury in coal

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**Abstract** A huge amount of coal is always stored in open spaces in coal-fired power plants before combustion. Mercury released from coal by rain or flowing water is an environmental risk and can cause contamination of the soil around the storage area. To better understand mercury pollution and to control mercury emission before combustion, it is necessary to determine the mobility and leaching characteristics of mercury from coal. In this study, we collected ten coal samples from one coal-fired power plant and proposed a sequential extraction procedure to get five fractions of mercury for evaluation. Elemental Hg was found as the most dominant fraction, and sulfate Hg was shown to be the second largest fraction. The mercury in the organic and the soluble fractions were not the major fractions, but they should still be considered because of their high mobility.

**Keywords** Mercury · Fractions ·  
Leaching characteristics · Coal ·  
Sequential extraction

## Introduction

Mercury is a toxic element and exhibits bioaccumulation, persistence, and long-distance transportation properties. Inorganic mercury can be methylated into organic forms (Jin et al. 2006; Chen et al. 2007) that are more toxic and can cause serious diseases (Liao et al. 2005). Therefore, it is important to study all possible types of mercury pollution in the environment. Coal always contains some mercury. Although the level of mercury in coal is not always high (in nanograms per gram), the total amount of mercury emitted by coal combustion is large because of large worldwide coal consumption. Coal-fired power plants play a major role in the consumption of coal, and coal will continue to be used as a method of power generation in the upcoming decades (Jiang et al. 2006), especially in developing countries. Coal-fired power plants can cause environmental mercury pollution because mercury is released from coal stored in open spaces that are exposed to water (rain or other sources) prior to combustion. The mercury released from coal can go into the soil or groundwater. In addition, coal is always cleaned by water to remove pollutants before combustion. This makes it necessary to investigate the existing forms and leaching characteristics of mercury in coal. This study can help in understanding the transportation and mobility of

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mercury in coal and may also be used to develop methods of mercury emission control.

To evaluate the mobility of mercury, many studies have been done on soil and sediment samples (Biester and Scholz 1997; Barnett and Turner 2001; Kot and Matyushkina 2002; Bloom et al. 2003; Sahuquillo et al. 2003; Kot 2004; Hall et al. 2005; Sanchez et al. 2005; Shi et al. 2005b). The use of sequential extraction procedures to characterize mercury into different chemical fractions is a popular method in these studies, and the fractions represent different physical and chemical forms of mercury (Sahuquillo et al. 2003; Hall et al. 2005; Shi et al. 2005a; Noel et al. 2007). Even though the methodology has been applied to many different samples, there are few applications to coal (He et al. 2006; Zheng et al. 2008). We apply these methods to coal to evaluate the mobility of mercury from coal and to understand the transportation properties of mercury in coal. The objective of this study is to propose a modified sequential extraction method and to characterize the operational species of mercury in coal. This will aid in understanding the leaching characteristics and mobility of mercury in coal.

## Materials and methods

### Reagents

Deionized water supplied by EASYpure LF System (18.2 M $\Omega$ ; Model D7382-33, Barnstead Thermolyne, USA; <http://www.barnsteadthermolyne.com/>) was used throughout the experiments. Nitric acid, potassium hydroxide, hydrochloric acid, acetic acid, and ammonium chloride (analytical grade; Beijing Chemical Factory, People's Republic of China; <http://www.crc-bj.com/>) were used for extraction and digestion. Mercury standard solutions were prepared in deionized water from a mercury stock solution (National Standard Material Research Center, People's Republic of China; <http://www.nrccrm.org.cn/>).

### Instrumentation

An atomic fluorescence spectrometer (Suzhou QingAn Instrument, People's Republic of China;

<http://www.greencalm.com/>) was used to determine mercury. A horizontal rotary shaker was used to perform the extraction process and a pH meter was used to measure pH values. All glass containers used were soaked in 50% HNO<sub>3</sub> (v/v) and rinsed with deionized water three times before use. The extracts were stored in plastic tubes in dark, cool conditions prior to analysis.

### Sample collection

Ten coal samples were collected from one coal-fired power plant in Northern China, which has been actively running for more than 30 years. The coal samples were from different coal mines in Northern China and are always mixed together for combustion. Ten finely ground coal samples were collected before being mixed. Approximately 1.0 kg of coal was taken for each sample. The coal samples were zipped into plastic bags and transported to the laboratory directly. The coal samples were sieved through 80-mesh sieves for use.

### Sequential extraction procedure

A modified five-step extraction procedure (Sladek and Gustin 2003; Liu et al. 2006) was used in this experiment. The chemical fractions of mercury in the coal samples were divided into water-extractable Hg (F1), acid-soluble Hg (F2), organic matter-bound Hg (F3), elemental Hg (F4), and sulfide Hg (F5). The definitions of each fraction and chemical compositions applied are listed in Table 1. One gram of coal sample was weighed and placed into a 50-mL centrifuge tube. Twenty milliliters of extractant was added for each step. The residue from each step was used in the next extraction step after washing two times with deionized water. Mercury in the extract from each step was determined by atomic fluorescence spectroscopy.

### Analysis of total Hg in coal

A 0.1-g coal sample was weighed into a 25-mL beaker, and 20 mL of aqua regia was added. After predigestion at room temperature, the sample was heated in a water bath at 60°C for 12 h. The

**Table 1** Definition of fraction and sequential extraction procedure used in experiment

Extraction step	Fraction ID	Extractant	Extraction process	Fraction definition
1	F1	0.5 M NH <sub>4</sub> Cl	Room temperature, shaking for 24 h	Ion-exchangeable Hg
2	F2	0.1 M CH <sub>3</sub> COOH + 0.01M HCl	Room temperature, shaking for 24 h	Acid-soluble Hg
3	F3	1 M KOH	Room temperature, shaking for 24 h	Organic matter-bound Hg
4	F4	12 M HNO <sub>3</sub>	Room temperature, shaking for 24 h	Elemental Hg
5	F5	Aqua regia	Room temperature, static, 12 h; heating at 60°C in water bath for 12 h	Sulfide Hg

digested sample was then transferred into a 50-mL centrifuge tube and was centrifuged at 4,000 rpm for 15 min. The supernatant was then analyzed for the determination of total mercury. To control the quality of the analytical process, the procedure was simultaneously performed on the Standard Reference Method (SRM) material GBW08302. The average recoveries of Hg in the SRM material were 86.2–112% ( $n = 3$ ). The detection limit of mercury by the instrument was 0.05 ng/mL. These results indicated that the total analysis of Hg was reliable and precise enough for our study.

**Results and discussion**

**Total Hg in coal**

The total content of Hg in the coal samples was in the range of 264–587 ng/g (Fig. 1). The average value of total Hg was 395 ng/g. This value was higher than that in a previous report about coal in China (Zheng et al. 2008). This is probably because the coal samples studied in our experiment

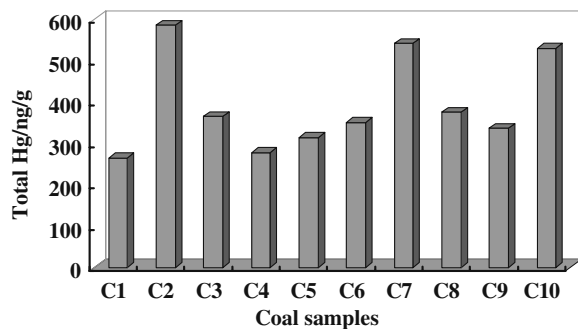
were from Northern China, which is not representative of the coal used in other power plants across the country. It is necessary to characterize the species of Hg in coal for a better understanding of its mobility and leachability, which will help control mercury pollution in the future.

**Operational species of Hg in coal**

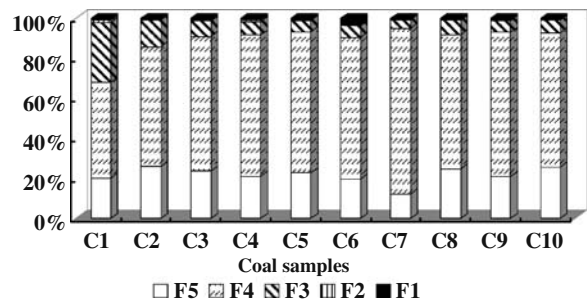
Mercury extracted by each extraction step was labeled as F1, F2, F3, F4, and F5, which represented the different forms associated with the different phases in coal. The distribution patterns of different species in each sample is shown in Fig. 2.

*Ion-exchangeable Hg (F1)*

To further understand the mobility of mercury in coal, a sequential extraction method was established and applied to assess the leaching characteristics of mercury. The sequential extraction procedure operationally defined mercury as various species (Liu et al. 2006). In our study, mercury in coal was divided into five fractions. The first two



**Fig. 1** Total mercury in the coal samples



**Fig. 2** Distribution of mercury in different fractions in the coal samples

fractions (F1 and F2) were the more important fractions because of their high mobility compared to the other fractions. The operational fractions were defined by the selective extraction procedure rather than by the naturally occurring forms. The most labile fraction was the ion-exchangeable fraction, F1. Mercury in this fraction had high mobility and leachability under natural conditions, and it is easily leached into the environment to take part in biogeochemical cycling. To obtain the mercury content in this fraction, we performed an extraction with 0.5 M  $\text{NH}_4\text{Cl}$ . It has been reported that  $\text{NH}_4\text{Cl}$  can be used to selectively extract the ion-exchangeable or soluble mercury present in a solid phase. (Sladek and Gustin 2003). In our experiment, 20 mL of 0.5 M  $\text{NH}_4\text{Cl}$  solution was used to extract Hg in coal. The dissociation of  $\text{NH}_4^+$  from  $\text{NH}_4\text{Cl}$  could provide an exchanging cation for soluble Hg ( $\text{Hg}^{2+}$ ) in the matrix. The presence of  $\text{Cl}^-$  in the solution also helped to complex Hg with  $\text{Cl}^-$ .  $\text{NH}_4^+$  and  $\text{Cl}^-$  or other similar ions are found in all natural bodies of water. Extracting the ion-exchangeable Hg by  $\text{NH}_4\text{Cl}$  could indicate the possible leachability of Hg in coal by water under natural conditions. The content of Hg in this fraction ranged from 2.27 to 10.8 ng/g (Table 2). The F1 fraction accounted for 1.0% to 3.2% of the total Hg (Fig. 2). The results indicated that the amount of Hg in the ion-exchangeable fraction was low. The results showed that it was difficult to extract or rinse out Hg from the coal samples by water or a salt solution under naturally occurring conditions.

### Acid-soluble Hg (F2)

The fraction labeled F2 was the second most labile fraction. The mixed acid solution (0.1 M  $\text{CH}_3\text{COOH}$  and 0.01 M  $\text{HCl}$ ) was used to extract the acid-soluble mercury in the coal samples. This could simulate human stomach acid (Liu et al. 2006). The acid mixture was used to evaluate the leachability of mercury from coal samples by weak acid, not to simulate stomach acid. Hg in this fraction was regarded to be sensitive to pH. Carbonate or other soluble salts in this fraction could be dissolved by weak acid. Mercury in this fraction could be leached out into water easily when conditions become acidic. Only 1.61 to 2.65 ng/g Hg was found in the F2 fraction (Table 2). The proportion in this fraction was only 0.3–1.2% of the total amount of Hg (Fig. 2). These results demonstrated that the Hg in coal was not sensitive to extraction by weak acid.

### Organic matter-bound Hg (F3)

During the process of coal formation under the Earth's surface, mercury could react with organic substances to form stable complexes or compounds. Mercury in this fraction is more stable than the Hg in the first two fractions (F1 and F2; Wallschläger et al. 1998). Mercury in this fraction has limited mobility and bioavailability and is not as sensitive to environmental conditions as the Hg in F1 and F2. Due to this insensitivity, Hg is more stable and does not participate

**Table 2** Different fractions of Hg in coal samples (in nanograms per gram,  $n = 3$ )

Coal sample	F1	F2	F3	F4	F5	Sum <sup>a</sup>	Total	Recovery <sup>b</sup> (%)
C1	2.27 ± 0.15	2.65 ± 0.22	68.4 ± 3.5	109 ± 6.1	46.4 ± 2.6	228	264 ± 25	86
C2	3.19 ± 0.21	1.94 ± 0.15	88.3 ± 4.6	389 ± 18	170 ± 9.0	653	587 ± 62	111
C3	3.30 ± 0.19	1.67 ± 0.13	25.3 ± 2.2	221 ± 15	77.8 ± 4.1	329	366 ± 38	90
C4	3.02 ± 0.28	1.74 ± 0.20	21.3 ± 1.9	217 ± 15	65.4 ± 5.2	308	278 ± 20	111
C5	3.02 ± 0.20	1.61 ± 0.15	20.0 ± 1.6	256 ± 14	82.6 ± 5.5	363	314 ± 31	116
C6	10.8 ± 0.95	1.61 ± 0.12	20.0 ± 2.1	238 ± 17	67.0 ± 5.0	338	351 ± 42	96
C7	2.43 ± 0.12	1.74 ± 0.11	24.3 ± 2.6	492 ± 28	73.7 ± 4.2	594	543 ± 63	110
C8	2.59 ± 0.32	1.67 ± 0.12	30.3 ± 2.8	289 ± 21	107 ± 6.0	430	376 ± 51	114
C9	2.43 ± 0.21	1.87 ± 0.14	23.1 ± 1.8	280 ± 11	81.1 ± 4.5	388	336 ± 41	115
C10	2.70 ± 0.17	1.81 ± 0.16	30.1 ± 2.4	326 ± 18	125 ± 8.0	486	530 ± 43	92

<sup>a</sup>Sum = F1 + F2 + F3 + F4 + F5

<sup>b</sup>Recovery = sum/total

much in biogeochemical cycling. However, mercury in this fraction would become labile when the oxidation–reduction conditions are changed. Under oxidizing or strongly basic conditions, the organic binding structures and other reducing compounds could be destroyed and the mercury associated with them could be leached out into the environment. Mercury in this fraction has always acted as a sink and reservoir for mercury emission. It has been reported that 1 M KOH was strong enough to break the complex of mercury with organic matter in soil (Liu et al. 2006); 1 M KOH was also used to extract the Hg bound to organic matter in this work. The amount of mercury in the F3 fractions is shown in Table 2. The content ranged from 20.0 to 88.3 ng/g. Mercury present in this fraction was 5.5–30% of the total Hg in the coal samples (Fig. 2). The results indicated that a notable part of Hg was present in the organic matter-bound fraction.

#### *Elemental Hg (F4)*

HNO<sub>3</sub> (12 M) was used to extract mercury into the elemental fraction according to previous reports (Bloom et al. 2003; Kocman et al. 2004; Liu et al. 2006). The content of mercury in this fraction ranged from 109 to 492 ng/g (Table 2), corresponding to 48–83% of the total amount of mercury in the coal (Fig. 2). This fraction had the highest abundance of Hg. This means that most of the mercury in coal was present as elemental Hg and could be extracted by strong acid (12 M HNO<sub>3</sub>). The amount of mercury in this fraction in coal was very similar to that in soil (Liu et al. 2006). In polluted soil, mercury in this fraction was also abundant. Mercury in coal was sensitive to strong acid, and this property may be useful for coal cleaning in the future.

#### *Sulfide Hg (F5)*

Mercury has a strong affinity for sulfide. During the process of coal formation, mercury could bind with sulfide to form compounds such as HgS and Hg<sub>2</sub>S. These kinds of mercury compounds are difficult to dissolve under natural conditions. The species of mercury in this fraction were always regarded as the residue fraction. Mercury in this

fraction is not hazardous to the environment because of its low mobility and bioavailability. To leach elements from this fraction was very difficult because the structure of the crystalline lattice had to be sufficiently destroyed by strong acid or base. In our paper, aqua regia was used. The amount of mercury in this fraction ranged from 46.4 to 170 ng/g (Table 2), corresponding to 20% to 26% of the total amount (Fig. 2). Mercury in this fraction could also be burned and emitted into the atmosphere during the combustion process, contributing to the global pollution of mercury.

#### Mass balance

To evaluate the accuracy of the sequential extraction procedure and to make sure there was no obvious loss of analytes during the process, the mass balance was calculated. The recoveries were calculated by comparing the sum of various fractions with the total content in the samples. The recoveries are shown in Table 2. The sum of fractions extracted by each step was in good agreement with the amount from the digestion procedure by aqua regia. The recoveries obtained were from 86% to 116%. This means that there was no obvious loss of mercury during the analysis and pretreatment process.

#### Conclusions

The amounts of mercury in the coal samples studied in this experiment were in the range of 264–587 ng/g. The average content was 395 ng/g. Mercury in coal was characterized as five fractions, using the sequential extraction procedure. Mercury in the different operational fractions indicated different mobility and leachability. The results from our experiments indicate that most of mercury in coal was present in the elemental fraction, which could be extracted with a strong acid. Although the most labile fractions (F1 and F2) contained only a small part of the total mercury in the coal samples, leaching of mercury from coal in open storage should also be considered because of the large use of coal in power plants and the high toxicity of mercury.

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