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Stone coal as a potential atmospheric mercury source in Da-Ba-Shan mountain areas, China

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ABSTRACT

Mercury (Hg) emissions from stone coal that formed from marine lower organisms in the late Proterozoic and early Paleozoic have not been paid much attention in China. In this research, Hg concentrations in different fueled coals (stone coal, humic coal) and charcoal that derived from wood and paired slags, atmospheric Hg emissions and atmospheric Hg levels were studied in Shaanxi province, China. The average Hg concentration in stone coal produced in Da-Ba-Shan mountain areas in Southern Shaanxi was 539.4 $\mu g \cdot kg^{-1}$, about 15 and 38 times higher than that of humic coal (36.0 $\mu g \cdot kg^{-1}$) and charcoal (14.2 $\mu g \cdot kg^{-1}$), respectively. Atmospheric Hg emission usually lasted for 2–3 h after fueling stone coal, with the majority of Hg emitted during the first 1 h. 95.5–99.4% of Hg in the fuel would be lost into the atmosphere for three types of fuels. Mercury emission factor (MEF) of stone coal was 40–120 times higher than those of humic coal and charcoal based on heat value. Average atmospheric Hg concentration at 0.5 m above the stove could reach 1600–2000 $ng \cdot m^{-3}$ if burning stone coal, which exceeded the standards for residential ambient air (200–300 $ng \cdot m^{-3}$) by 5–10 times and also was nearly two orders of magnitude higher than that of burning humic coal (20–60 $ng \cdot m^{-3}$). Health risk would be a concern for local residents who depend on stone coal for cooking and heating but without any control measures of flue gas. In Shaanxi province alone, Hg emission through domestic combustion of stone coal was estimated to be 1.34 Mg in 2011. Higher mercury emission amounts are possible in southern China where stone coal has been intensively used. Total mercury emissions from this source category need to be further investigated on the national scale.

1. Introduction

A large amount of coal is produced and consumed in China on daily basis (Bai et al., 2018; Dai and Finkelman, 2018). Coal combustion has become one of the major anthropogenic sources emitting mercury (Hg) into the atmosphere (UNEP, 2002; Streets et al., 2011), which has drawn much attention in establishing or proposing Hg emission control polices. Stone coal has been neglected for its potential capacity in Hg emission. For example, Hg emission from coal combustion was estimated to be 253.8 Mg (10^6 g) in China in 2010, accounting for 48% of the total Hg emission (Zhang et al., 2015). Among this, 20.7 Mg (or 4% of the total mercury emissions) was from residential coal combustion (Zhang et al., 2015). However, the calculation of Hg emissions from coal combustion was based on the emission factors of humic coal, that formed from higher plants which colonized the land after Devonian (Li et al., 2018), without consideration of the much higher Hg contents in stone coal.

Stone coal, also referred to as stone-like coal, is a black, combustible, low-heat value, high-rank sedimentary rock mainly derived from the late Proterozoic and early Paleozoic fungi and algal-type plants after saprofication and coalification in a marine-influenced environment, such as epicontinental sea, lagoon or bay (Dai et al., 2018). The age of stone coal spans from the late Proterozoic to middle Devonian, with the early Cambrian and Ediacaran (Sinian) stone coals are most widely distributed (GRI-CSA, 1982; Dai et al., 2018). It is characterized by high ash yields (generally in the range of 70–88%), lower organic carbon contents (15–25% on average), higher sulfur (usually 2–5% and up to 13.5%) and low heat values (generally 3.5–10.5 MJ/kg) relative to common coals (GRI-CSA, 1982; Piao, 1988; Dai et al., 2018). The metamorphic degree of stone coal is similar to that of anthracite coal (Jin et al., 2006; Luo, 2011). A large number of trace elements, such as As, Se, F, S, Hg, Pb, Cr, Cd, Zn, V, Cu, U, Mo and rare earth elements,

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are enriched in stone coal compare to humic coal (Jiang et al., 1994; Luo, 2011; Du et al., 2017; Dai et al., 2018), and stone coal has become a potential economic source for critical elements like V, Se, Mo and platinum group elements (Dai et al., 2018). For example, stone coal represents 87% of national V resource in China (118×10^{12} g as V_2O_5, GRI-CSA, 1982; Dai et al., 2018). However, some toxic elements in stone coal could be released into atmosphere during the combustion process and subsequently cause detrimental effects to humans and ecosystems (Zheng et al., 1999; Bai et al., 2006; Luo, 2011).

Mercury is one of the elements enriched in stone coal (Piao, 1988; Luo, 2011), and has been regarded as one of the most toxic heavy metal and listed as a priority contaminant by international organizations, such as United Nations Environment Programme and World Health Organization (UNEP, 2013; WHO, 1991). Mercury in air exists as gaseous elemental mercury (GEM, Hg^0, > 90% of the total Hg) and oxidized Hg (Hg^{2+}), with Hg^0 being able to travel globally due to its long life time (Schroeder and Munthe, 1998). Mercury could enter into aquatic and terrestrial systems either through atmospheric deposition or direct release from industrial waste water/solids, and deteriorate the environmental quality (Renzoni et al., 1998; Wright et al., 2018). The atmospheric Hg sources include natural, anthropogenic and re-emission sources (Pirrone et al., 2010). The natural sources are geogenic that include volcanic eruption, crustal weathering, thermal spring emissions, etc. (Pirrone et al., 2010); the anthropogenic sources include fossil fuel (coal, petroleum and gas) combustion, nonferrous metal smelting, cement production, waste incineration, etc. (Zhang et al., 2017); while, the re-emission sources include marine/soil emissions and burning of biomass (Eckley et al., 2015; Zhu et al., 2018). China and other Asian countries contributed the majority of anthropogenic Hg during the past three decades (Streets et al., 2011; UNEP, 2002, 2013). Coal combustion, lead/zinc smelting and cement industry are the three major source factors in China (Zhang et al., 2015; Wu et al., 2016).

Stone coal is far less widely utilized than humic coal due to its low heat value and high ash yield. However, it is indeed widely used for cooking and heating in residential houses, particularly in mountain areas in southern China where stone coal is abundant and cheap, while the high quality and expensive humic coal is scarce (Dai et al., 2018). Stone coal has not been included in the coal-related statistical yearbook (China energy statistical yearbook, 2017), and has been omitted from the Hg emission database. It is reported that the stone coal reserves are up to 61.8×10^9 Mg in China and is widely distributed in southern China (Fig. 1A), such as in Hunan (18.7×10^9 Mg), Zhengjiang (10.6×10^9 Mg), Anhui (7.5×10^9 Mg), Jiangxi (6.8×10^9 Mg), Hubei (2.5×10^9 Mg) and Shaanxi (1.5×10^9 Mg) (GRI-CSA, 1982; Dai et al., 2018). The most abundant reserve is in the south of Qin-Ling Mountain areas (32.1×10^9 Mg), including the southern Shaanxi, northwestern Hubei, western Hunan and northern Chongqing (GRI-CSA, 1982). Southern Shaanxi is located in the Qin-Ling Mountain and the Da-Ba-Shan Mountain stone coal area (Fig. 1B) and is one of the most important areas burning the stone coal in China for the residential cooking, heating and lime calcining (Jin et al., 2006; Chen et al., 2010; Luo, 2011; Wang, 2011) due to the high quality of stone coal with lower ash yield, higher heat value and lower sulfur content compare to that mined from most other areas in China (GRI-CSA, 1982; Chen et al., 2010; Dai et al., 2018). However, owing to the lack of emission control measures in residential houses, burning stone coal for cooking and heating without chimney may release high concentrations of potentially toxic elements/compounds, such as As, F, CO, SO_2 and so on (Li et al., 2003; Bai et al., 2006; Jin et al., 2005; Luo, 2011). Poisoning accidents by high concentrations of F and As produced from stone coal combustion has been reported in this region since early 1980s (Hu et al., 1985; Zheng et al., 1999; Li et al., 2004). Concentrations of F in stone coal mined in Ankang city, located in southeastern Shaanxi, were mainly in the range of 600–2000 mg·kg^{-1} with the highest value of 4532 mg·kg^{-1} (Luo, 2011), and those of As were in the range of 26–234 (averaging at 108) mg·kg^{-1} (Shi et al., 2006). In comparison, the average content of F and As in Chinese coal was only 130 and 3.79 mg·kg^{-1}, respectively (Dai et al., 2012).

Although Hg is enriched in stone coal, very limited efforts have been devoted to understanding its concentration and atmospheric emission. Luo (2011) reported the average Hg content of 0.6–0.7 mg·kg^{-1} ($N = 27$) in stone coal in Ankang, southern Shaanxi province for different deposited periods and Shi et al. (2001) reported Hg of 0.45–0.93 mg·kg^{-1} ($N = 3$) in stone coal from western Zhejiang province. These values were 3–6 times higher than the Chinese coal (0.163 mg·kg^{-1}, Dai et al., 2012) and 2–4 times higher than the average value of global black shale (0.27 mg·kg^{-1}, Ketris and Yudovich, 2009). One laboratory study was conducted on stone coal combustion and heavy metal emissions from a circulating fluidized bed boiler and showed most Hg and Se were lost into flue gas during the combustion, while the vast majority of other metal(loid)s, such as Pb, Cd, Cr and As remained in the slags (Shi et al., 2001). Hg emission ratios as high as 52–99% were reported in residential stoves for humic coal combustion (Pyka and Wierzchowski, 2016; Wu et al., 2016; Cui et al., 2019). To fill the data and knowledge gaps related to stone coal Hg emissions, solid samples of stone coal, humic coal and charcoal derived from tree trunks and the corresponding slags were collected from domestic stoves/burners in central and southern Shaanxi province in China. Hg emission ratios and emission factors were then calculated. Meanwhile, Hg concentration in the air at 0.5 m above the stove was monitored for different fuels. Knowledge gained from the present study would improve the Hg emission estimates from this potential source sector.

2. Methods

2.1. Sample collection

In Shaanxi province, stone coal is mainly distributed in the southeast part, covering 9 counties or districts in the south Qin-Ling Mountain and north Da-Ba-Shan Mountain areas (Fig. 1), with a total reserve of 1.5×10^9 Mg (GRI-CSA, 1982), among this, about 80% is deposited in Ankang city and the rest is roughly evenly distributed in Hanzhong city and Shangluo city (Wang, 2011). 69% of the stone coal resources in Shaanxi were formed in the Silurian Period, while early Cambrian and other periods accounts for 15% and 16%, respectively (GRI-CSA, 1982), which is much different from the situation of the national stone coal that mainly formed in early Cambrian (GRI-CSA, 1982; Dai et al., 2018). Stone coal in Ankang was largely deposited in the central to southern prefecture of this city, such as Hanbin district, Ziyang county, Langao county, Pingli county and Zhenping county (Chen et al., 2010; Yang and Ma, 2013). Those formed in Cambrian are featured with low ash yield (20–40%) and high heat value (16.74–25.12 MJ·kg^{-1}), but the deposit scale is small. In contrast, those formed in Silurian are with high ash yield (40–90%) and low heat value (4.19–10.47 MJ·kg^{-1}), and the deposit scale is relatively large (Chen et al., 2010; Yang and Ma, 2013).

In this study, paired stone coals and the corresponding slags were sampled in Ankang city in winter 2011 to evaluate the Hg atmospheric emissions from this source (Table 1). Humic coal or charcoal that are also used for residential heating and cooking and their slags were collected in Xianyang, Hanzhong and Ankang city, from central to southern Shaanxi. A total of nine families was investigated in 2011, as indicated in Fig. 1 and Table 1. These families were chosen because of their fuel type use. In each family, about 0.5–1 kg of different feed fuels and their corresponding slags were collected. An additional 6 stone coal samples and 5 humic coal samples (each about 1 kg) from families in Shimen town, Yanmen town and Zuolong town in Langao county and Hanbin district in Ankang city, were obtained in winter 2012 to increase the fuel's representativeness and these were not shown in Fig. 1. All together, 14 samples of humic coal, 10 samples of stone coal and 2 samples of charcoal were collected in 2011 and 2012. Stone coal was produced locally in Ankang, while humic coal was mainly imported

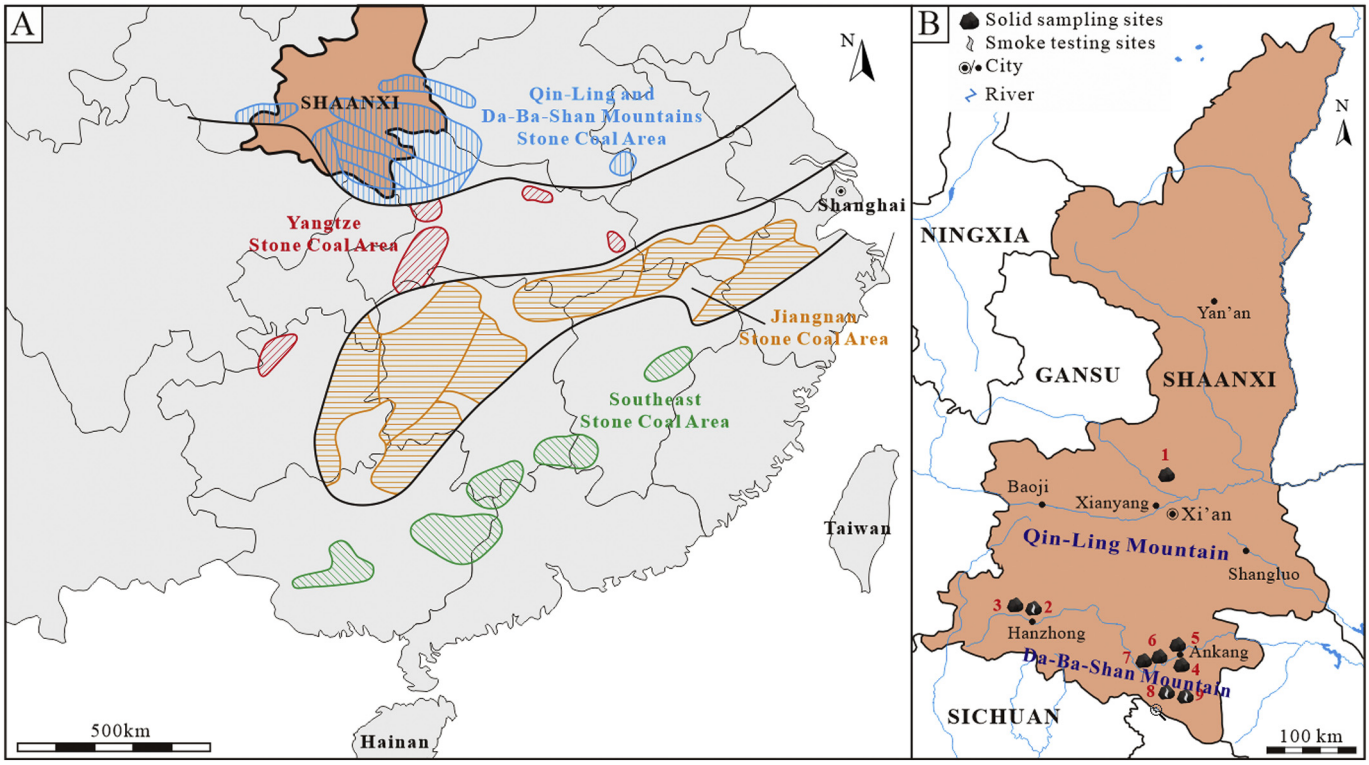

Fig. 1. (A) the distribution of stone coal resource in southern China based on GRI-CSA (1982), and (B) the sampling sites of families in Shaanxi province in 2011.

from Ningxia Hui autonomous region for use in Ankang and Hanzhong city or from northern Shaanxi for use in Xianyang city. Humic coal from both regions was formed in the early to middle Jurassic period. Charcoal used in local families in Ankang was derived from tree trunks of oak, beech and elm.

The fuel was burned indoor in fire pan (high quality humic coal or charcoal, Fig. 2A, B) or ground stove (stone coal, Fig. 2D,E), but some families had metal stove with chimney to burn bituminous coal produced in Ningxia or North Shaanxi (Fig. 2C). Stone coal stoves used by the local residents generally have the same design, with 15–20 cm in diameter and 0.8–1 m in depth of the hearth (Fig. 2D,E; also refer to Jin et al., 2005), which are dug into the ground, convenient for people to warm their feet and hands in winter, hence called ground stove. Ground stove is also used to cook the food and to boil the water on daily basis, and the stove pit sometimes is utilized for fermentation the rice wine due to its warmer temperature. Each time about 2 kg of lump stone coal with 2–5 cm in diameter was added into the stove, and the combustion usually lasted for 3 h before completely burned. For the iron stove burning humic coal (Fig. 2C), it is used for cooking the food and heating the room but not for heating feet and hand. The fir pan burns charcoal or high quality humic coal (Fig. 2A, B) and is primarily used for heating hands and feet, but not for cooking.

During coal combustion, Hg is emitted into flue gases in the forms of Hg^0, gaseous oxide mercury (Hg^{2+}) and particulate bound mercury (Hg^P) (Galbreath and Zygarlicke, 2000). Hg^{2+} and Hg^P are easily deposited nearby the emission sources through wet/dry deposition and impacted the local environment, while Hg^0 could be inhaled by the inhabitants and also transport a long distance and be a global concern (WHO, 2003; Schroeder and Munthe, 1998). Our recent study on residential humic coal combustion in Guizhou province, southwest China showed Hg in the exhausted flue gas was dominated by Hg^0 (91.2 ± 3.8%), followed by Hg^{2+} (7.6 ± 3.5%) and Hg^P (1.2 ± 1.7%) as determined by a wet chemistry method, namely Ontario Hydro Method (Cui et al., 2019). In the present study, continuous measurements of Hg^0 were conducted at 0.5 m height above different stoves/burners (including 2 ground stoves for stone coal, 1 fire pan and

Table 1
Locations of the investigated families and samples collected.

Family ID	Location	Sampling year	Sample types and numbers
1	Luqiao town, Sanyuan county, Xianyang city	2011	One humic coal from North Shaanxi and paired slag
2	Hantai district, Hanzhong city	2011	Two humic coals from Ningxia and paired slags, Hg^0 at 0.5 m above the iron stove
3	Hantai district, Hanzhong city	2011	Three humic coals from Ningxia and paired slags
4	Laocheng district, Ankang city	2011	One humic coal from Ningxia and paired slag; One charcoal and paired slag;
5	Jiangbei district, Ankang city	2011	One stone coal and paired slag
6	Wuli town, Hanbin district, Ankang city	2011	One humic coal from Ningxia and paired slag
7	Wuli town, Hanbin district, Ankang city	2011	One stone coal and paired slag; one charcoal and paired slag
8	Shimen town, Langao county, Ankang city	2011	One stone coal and paired slag, Hg^0 at 0.5 m above the ground stove; one humic coal from Ningxia and paired slag, Hg^0 at 0.5 m above the fire pan
9	Shimen town, Langao county, Ankang city	2011	One stone coal and paired slag, Hg^0 at 0.5 m above the ground stove
10–20	Langao county and Hanbin district, Ankang city	2012	6 local stone coal and 5 humic coal from Ningxia

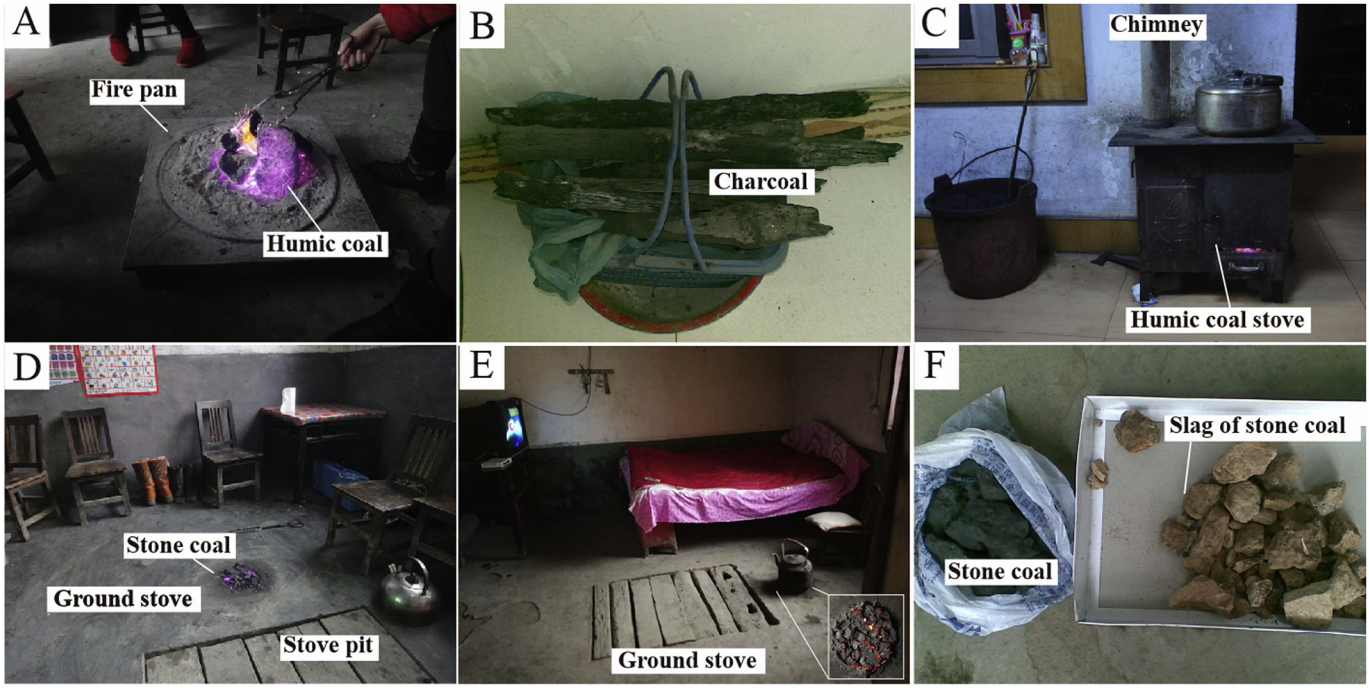

Fig. 2. On-site sampling of different types of solid fuels. (A), fire pan at family #8; (B), charcoal sample at family #4; (C), iron stove for humic coal at family #2; (D), ground stove at family #8; (E), ground stove at family #9; (F), stone coal and its slag.

1 iron stove for humic coal) in the houses of three families (No. 2, 8 and 9 as showed in Table 1) immediately after adding different fuels into the stove/fire pan. The chosen of these three families for Hg^0 monitoring is considered their convenience. The height of 0.5 m is roughly the breathing height of residents when they are sitting around the stove for heating and other activities, especially for the ground stove and fire pan. For the iron stoves that burning humic coal and equipped with a chimney venting flue gas to outside buildings, such as family No.2 (Fig. 2C), the chimney was intentionally removed from the stove for the Hg^0 measurement over the stove in order to assess the possible impact of such burners on indoor air quality. The locations and detailed sampling information of this research is summarized in Table 1.

2.2. Analysis methods and quality assurance

The solid samples were air dried, homogenized and ground to sizes smaller than 0.15 mm. The US EPA Method 7473 was adopted to determine Hg concentrations in solid samples, which heat solid samples at 800 °C and measure the released Hg^0 by cold-vapor atomic absorption spectrometry (CVAAS, Lumex RA915-Pyro 915, Lumex Ltd., Russia) with a detection limit of 0.1 $ng{\cdot}g^{-1}$. Each solid sample was determined at least three times to obtain a mean value. Certified reference material stands for coal (NIST 1630a, NIST 1632d) and fly ash (NIST 1633b) were used to guarantee the analytical quality, and the recovery of Hg was found to be in the range of 90.7–102.9% (Table 2).

Proximate analysis of different fuels was performed using the Chinese national standard method (GB/T 212-2008). Ultimate analysis (C, N and H) was accomplished by an elemental analyzer (vario MACRO cube, Elementar, Germany). For total sulfur in different kind of fuels, it was detected by the Eschka method according to GB/T 214-2007. Certified reference materials (GSB06-2105-2007 for anthracite and GSB06-2182-2008-1 for gangue) were detected along with stone coal, humic coal and charcoal samples at the same time, and the measured proximate and ultimate mean values were close to the certified contents and variation coefficients were lower than 5%.

Hg^0 in ambient air was directly measured online using a portable Lumex RA 915+ mercury analyzer and the data was recorded by a laptop computer at the same time. Before each measurement, the Lumex instrument was manually calibrated using its internal test cell. The limit of detection of the instrument is 0.3 $ng{\cdot}m^{-3}$ and one data point is collected per second (Ci et al., 2011).

3. Results and discussion

3.1. The physicochemical properties and Hg contents in different types of fuels

The proximate and ultimate analysis (Table 3) indicate that stone coal has distinctive properties compared to humic coal and charcoal, especially for ash yield and heat values. The extremely high ash yield (50.2–64.3%) and relatively low heat values (5.4–10.9 $MJ{\cdot}kg^{-1}$) of stone coal indicate it is indeed a type of low-grade fuel material and the stone coal samples in this study should be formed in Silurian according to the ash yield and heat value as aforementioned (Chen et al., 2010). The shape of stone coal slag remained that of the lump stone coal, namely, unchanged, but the color of the stone coal slag has changed from black for stone coal to dark red (Fig. 2F). While, for humic coal and charcoal, the ash yields were 8.1% and 3.4%, and the heat values

Table 2
Recovery of Hg of standard reference materials in this study.

Standard reference material	Determined value ($\mu g{\cdot}kg^{-1}$)	Certified value ($\mu g{\cdot}kg^{-1}$)	Recovery (%)
NIST 1630a Bituminous coal (N = 6)	96.5 ± 7.1	93.8	102.9
NIST 1632d Bituminous coal (N = 5)	84.2 ± 5.8	92.8	90.7
NIST 1633b Fly ash (N = 3)	138.0 ± 5.2	143.1	96.4

Table 3
Proximate and ultimate analysis of different fuels.

Fuel type	Family ID	Proximate analysis					Ultimate analysis				
		Mad (%)	*Aad* (%)	*Vad* (%)	FC*ad* (%)	*Qad,net,p* (MJ·kg^{-1})	*Cad* (%)	*Had* (%)	*Nad* (%)	*Oad* (%)	*Sad* (%)
Humic coal (N = 6)	#1	13.45	4.50	35.07	46.98	23.02	61.66	3.84	0.70	15.33	0.53
	#2	10.75	8.73	35.15	45.37	24.35	62.97	3.42	0.58	12.00	1.56
	#3	10.57	5.04	34.54	49.85	25.45	67.42	3.78	0.75	11.15	1.28
	#3	11.47	3.72	31.50	53.31	25.32	66.98	4.05	0.72	12.96	0.11
	#4	12.06	4.16	31.11	52.68	24.67	64.03	3.16	0.69	15.80	0.10
	#8	11.32	22.34	22.90	43.44	19.24	52.04	2.68	0.59	10.95	0.10
	Min-Max	10.57–13.45	3.72–22.34	22.9–35.15	43.44–53.31	19.24–25.45	52.04–67.42	2.68–4.05	0.58–0.75	10.95–15.8	0.10–1.56
	Mean ± SD	11.60 ± 1.05	8.08 ± 7.21	31.71 ± 4.67	48.61 ± 4.00	23.68 ± 2.34	62.52 ± 5.6	3.49 ± 0.51	0.67 ± 0.07	13.03 ± 2.09	0.61 ± 0.65
Charcoal (N = 2)	#4	10.54	3.46	11.40	74.60	28.16	62.89	0.73	0.46	21.88	0.05
	#7	11.42	3.35	12.63	72.60	27.93	58.89	0.51	0.25	25.51	0.06
	Mean ± SD	10.98 ± 0.62	3.41 ± 0.07	12.01 ± 0.87	73.60 ± 1.41	28.04 ± 0.16	60.89 ± 2.83	0.62 ± 0.15	0.36 ± 0.14	23.69 ± 2.57	0.05 ± 0.01
Stone coal (N = 3)	#5	0.55	64.33	4.66	30.47	5.36	32.61	0.30	0.26	1.05	0.90
	#7	0.53	62.31	4.48	32.68	9.54	34.78	0.47	0.35	0.47	1.10
	#8	0.44	50.16	7.72	41.68	10.88	45.65	0.41	0.41	2.31	0.62
	Min-Max	0.44–0.55	50.16–64.33	4.48–7.72	30.47–41.68	5.36–10.88	32.61–45.65	0.3–0.47	0.26–0.41	0.47–2.31	0.62–1.1
	Mean ± SD	0.51 ± 0.06	58.93 ± 7.66	5.62 ± 1.82	34.94 ± 5.94	8.59 ± 2.88	37.68 ± 6.99	0.39 ± 0.09	0.34 ± 0.08	1.28 ± 0.94	0.87 ± 0.24

Note: M, moisture; A, ash; V, volatile; FC, fixed carbon; $Q_{net,p}$, net heat value at constant pressure; C, carbon; H, hydrogen; N, nitrogen; O, oxygen; S, sulfur; subscript "*ad*", air-dried basis.

were 23.7 MJ·kg^{-1} and 28.0 MJ·kg^{-1}, respectively, suggesting they were both low ash and high heat value fuels. The slags of humic coal and charcoal were in grey fine powders that completed disintegrated from the original fuels. Stone coals also had lower moisture (0.4–0.6%) and volatile matter (4.5–7.7%) than humic coal and charcoal, indicating they belong to anthracite coal.

Hg contents (Table 4 and Fig. 3) in stone coal were in the range of 219–1175 μg·kg^{-1} (mean: 539.4 ± 258.8 μg·kg^{-1}, $N = 10$), much higher than those of humic coal (5.4–169.0 μg·kg^{-1}, mean: 36.0 ± 42.9 μg·kg^{-1}, $N = 14$) and charcoal (2.4–26 μg·kg^{-1}, mean: 14.2 ± 16.7 μg·kg^{-1}, $N = 2$). Hg contents in stone coal found in the present study are slightly lower than those found by Luo (2011) for stone coal formed in the same period of Silurian (mean: 700 μg·kg^{-1}, range: 200–1900 μg·kg^{-1}, $N = 12$, Table 4) that collected from a broader geographic area in Ankang. Compared with the raw materials, Hg contents in slag of all kind of fuels (Table 4) were very low, with mean values of 2.8, 1.8 and 5.1 μg·kg^{-1} for stone coal, humic coal and charcoal, respectively. There are large differences in Hg contents between stone coal and humic coal produced in Shaanxi province or other parts of China (Zhang et al., 2012; Luo, 2011). Hg concentrations in stone coal found in this study are 1–7 times higher than the average Chinese humic coal (163 μg·kg^{-1}, Dai et al., 2012). High Hg in stone coal was ascribed to the scavenging of Hg from seawater by ancient microorganism (over 400 million years ago) that have high bio-productivity in the photic zone, followed by the advanced decay of biomass and remineralization under anoxic to euxinic conditions combined with very low clastic input, which finally led to enrichment of Hg and a broad spectrum of other redox-sensitive and biogenic metals in stone coal (Yin et al., 2017).

Mercury emission ratio (MER) was calculated according Eq. (1),

$$MER = \frac{C_{fuel} \times M_{fuel} - C_{slag} \times M_{fuel} \times A_{ad}}{C_{fuel} \times M_{fuel}} \times 100\% = \frac{C_{fuel} - C_{slag} \times A_{ad}}{C_{fuel}} \times 100\% \quad (1)$$

where C_{fuel} and C_{slag} are Hg concentration in different fuels and the corresponding slags (μg·kg^{-1}), respectively; M_{fuel} is the mass of different fuel burnt (kg); and A_{ad} is the ash yield (%) of different solid fuels based on air-dried masses.

Nearly all (95.5–99.4%) Hg was emitted into the atmosphere during fuel combustion in residential stoves regardless of solid fuel type (Table 4). No differences were found in MER of stone coal (99.2%), humic coal (99.4%) and charcoal (95.5%). These MER values were also comparable to those found for humic coal stoves in Guizhou (99.6%, Cui et al., 2019) and coal-fired power plants (92.2–99.9%, Table 4). Note that flue gas control measures, such as electrostatic precipitator (ESP), fabric filter (FF), and flue gas desulfurization (FGD) and denitrification, that have been widely installed in coal-fired power plants (CFPPs) in China for controlling particulate matter, SO_2 and NOx, have also achieved substantial synergistic Hg removals (Zhao et al., 2018; Tang et al., 2016). However, similar practices have not been enforced in residential coal combustion, resulting in flue gas discharged near the surface and causing direct impact on ambient environment and human health (Finkelman et al., 1999; Zheng et al., 1999).

3.2. Hg concentration in ambient air

Hg^0 concentrations in ambient air at 0.5 m above the stove are shown in Fig. 4 and Table 5. More than 3 h monitoring of the stone coal combustion covering the whole combustion process of a batch of fuel at family #8 in Langao county, indicated that Hg concentration increased rapidly at the initial stage of combustion (up to 16,377 ng·m^{-3}, Fig. 4A and Table 5), followed by a slow declining trend. The mean Hg concentrations were 2023 ± 2526 ng·m^{-3}, 431 ± 614 ng·m^{-3} and 74 ± 67 ng·m^{-3} for the first and high atmospheric Hg level period (0–70 min), the second and declining phase (70–117 min) and the last

Table 4
Hg concentration of solid samples and Hg emission ratio after combustion.

Sample type	Hg concentration (μg·kg^{-1})			Mercury emission ratio (%)	References
	Min	Max	Mean ± (SD)		
Humic coal (N = 14)	5.4	169.0	36.0 ± 42.9	99.38	This study
Slag(*N* = 9)	0.6	4.2	1.8 ± 1.1		
Charcoal (N = 2)	2.4	26	14.2 ± 16.7	95.52	This study
Slag (N = 2)	2.0	7.6	5.1 ± 3.5		
Stone coal (N = 10)	219	1175	539.4 ± 258.8	99.22	This study
Slag (*N* = 4)	0	6.65	2.8 ± 3.1		
Stone coal (Silurian, N = 12)	200	1900	700	/	Luo, 2011
Stone coal (Cambrian, N = 15)	200	1900	600	/	
Humic coal (Shaanxi)	9.0	1134.0	248.0	/	Zhang et al., 2012
Humic coal (China)	8.0	2248.0	170.0	/	
Humic coal (China, *N* = 1666)	/	/	163	/	Dai et al., 2012
Humic coal (Clarke value of world coal)			100 ± 10	/	Yudovich and Ketris, 2005
Humic coal (Thermal power plants, before APCD, N = 4)	163	311	213.8 ± 66.4	92.28 (90.61–93.63)	Wang and Luo, 2017
Humic coal (Coal-fired power plants, before APCD, N = 6)	9.5	281	143.8 ± 106.6	98.8–99.98	Zhang et al., 2008
Residential humic coal combustion in Guizhou, China (N = 27)	14	1050	370 ± 291	99.63 (96.2–100)	Cui et al., 2019

Note: APCD, air pollution control devices.

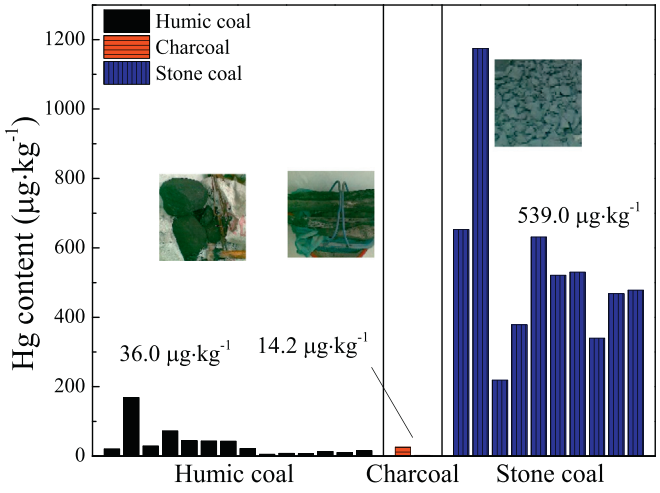

Fig. 3. Hg contents in humic coal, charcoal and stone coal used in this study.

and low level period (117–195 min), respectively. A similar situation was found for another ground stove at family #9 (also in Langao county, Fig. 4B and Table 5), with mean Hg concentrations of 2416 ± 3748 and 67 ± 66 ng·m^{-3} for the first period (0–18 min) and the last combustion period (180–192 min), respectively. Stone coal will break or crack during the combustion process, resulting in a large fluctuation in Hg concentration in ambient air during the first period (Fig. 4A,B), noting the peak value of 22,691 ng·m^{-3} at family No.9.

An earlier study by Liu et al. (2009) suggested that mercury emission from coal combustion was temperature dependent, e.g., little, majority, and almost all of Hg in coal would be lost when temperature is < 250 °C, in the range of 250–650 °C, and > 850 °C, respectively. The temperature of domestic stoves could reach up to 840–1060 °C (Yu et al., 2004) and last for 3 h, hence Hg in stone coal was expected to be emitted into the atmosphere completely. The gradually heating of stone/humic coal from the bottom layer to the upper layer of newly added fuel in the hearth will successively liberate Hg in fuels into ambient atmosphere, as indicated in Fig. 4. The Hg emission process, with the most emissions occurred in the first 1 h, was different from that of arsenic, that peaked at 3 h after the feeding stone coal, namely, the last combustion period (Tang, 2008). The average emission ratio of Hg (99.2%, this study) was much higher than that of arsenic (47%, Tang, 2008), and slightly higher than that of fluorine (80.6%, Yu et al., 2004) and selenium (73–98%, Fang et al., 2003) from stone coal combustion.

Hg contents in humic coal (36.0 ± 42.9 ng·g^{-1}) are about 15 times lower than those in stone coal (Fig. 3). As a result, the average Hg^0 concentrations at 0.5 m above the fire pan and humic coal stove were 60 ± 53 ng·m^{-3} and 20 ± 23 ng·m^{-3}, respectively, in the first stage immediately after feeding the fuel (Fig. 4C, D and Table 5). These figures should represent the highest values for these two types of fuel, but still much lower than those from stone coal combustion.

In the tested families, stone coal was burnt directly in the living room (Fig. 2d) or in the bed rooms (Fig. 2E) with ground stoves, with chimney being only applied in some humic coal stoves (Fig. 2C). Hence, high Hg^0 in indoor air would be a possible health concern, especially for the ground stove where the inhabitants sitting around for heating and other activities. The environmental standards for inhalation exposure to mercury vapor is 300 ng·m^{-3} in residential areas in China (TJ36-1979), or 200–300 ng·m^{-3} in United States (US ATSDR, 1999; National Research Council, 2000). It was obvious that the levels of Hg^0 vapor above the humic stove or fire pan are much safer than that of ground stove burning stone coal, especially at the first stage of burning when Hg^0 concentration (average: 2000–2400 ng·m^{-3}) above the stone coal stove exceeds the standards by 5–10 times. Approximately 80% of inhaled elemental mercury will be absorbed through the lungs by rapid diffusion, and to a less extent by dermal absorption or absorptions through the gastrointestinal tract (WHO, 2003). Once inhaled into the lungs, elemental mercury vapours rapidly enter the bloodstream. The lipophilic nature of elemental mercury results in its distribution throughout the body, including the brain and placenta. Finally, the neurological and behavioral disorders in humans would occur (WHO, 2003).

To better understand the worst situation of burning stone coal in an unventilated circumstance, we estimated Hg^0 in indoor air in a closed space with Eq. (2):

$$C_{air}^{Hg} = \frac{M_{coal} \times C_{coal}^{Hg} \times MER_{Hg}}{V_{house}} = \frac{M_{coal} \times C_{coal}^{Hg} \times MER_{Hg}}{S_{house} \times H_{house}} \quad (2)$$

where C_{air}^{Hg} is the Hg^0 concentration in indoor air (μg·m^{-3}); M_{coal} is the mass of stone coal added into the stove each time (kg); C_{coal}^{Hg} is the Hg concentration of stone coal (μg·kg^{-1}); MER_{Hg} is the emission ratio of Hg (%) calculated in Eq. (1); and V_{house}, S_{house} and H_{House} are the volume (m^3), ground area (m^2) and height (m) of the residential houses, respectively. C_{coal}^{Hg} and MER_{Hg} refer to the results of experimental analysis shown in Table 4, namely 539.4 μg·kg^{-1} and 99.22%, respectively. M_{coal} and H_{house} from the investigated families are relatively stable, with a value of ~2 kg and 3 m respectively, but S_{house} varied substantially (10–45 m^2).

The estimated ambient Hg concentration in a closed space is shown

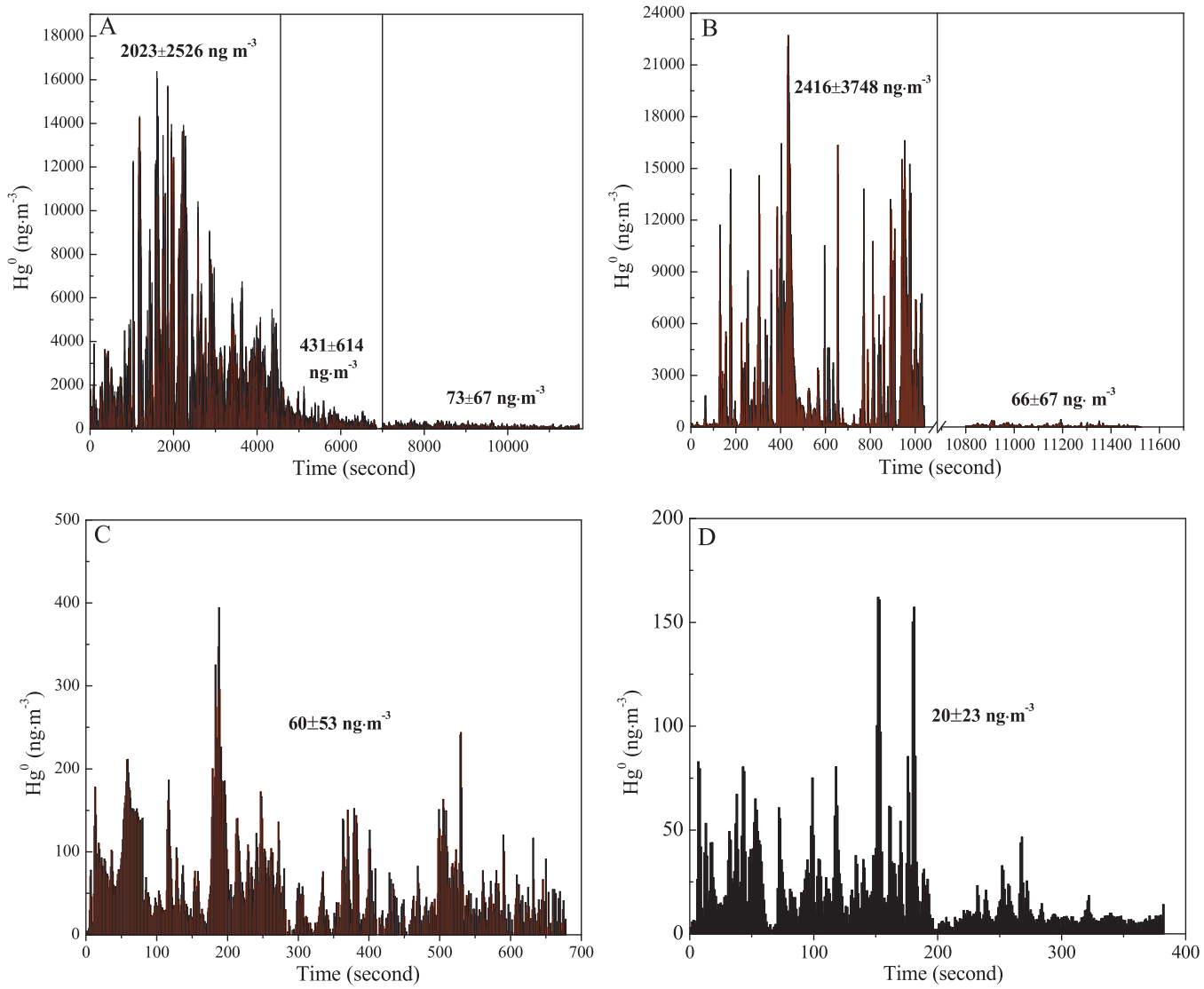

Fig. 4. Atmospheric Hg^0 concentration at 0.5 m above the stoves after adding the fuels. (A), Ground stone coal stove at family #8; (B), Ground stone coal stove at family #9; (C), Fire pan for humic coal at family #8; (D), Iron stove for humic coal at family #2 when the chimney was intentionally removed.

in Fig. 5. It can been seen that serious Hg pollution in air (20–50 $\mu g \cdot m^{-3}$) is possible if stone coal is burned without chimney and ventilation, noting that the standards for Hg in the residential atmosphere is only 200–300 $ng \cdot m^{-3}$ in China and USA (TJ36-1979; US ATSDR, 1999; National Research Council, 2000), or 20 $\mu g \cdot m^{-3}$ in workshop for occupational exposure in China (GB 16227-1996) and 50 $\mu g \cdot m^{-3}$ for occupational exposure in USA (US NIOSH, 2007). Such a polluted situation can happen frequently in the houses of stone coal users because of the absence of chimney and direct discharge of smoke into the indoor air. In southern Shaanxi, stone coal burning has resulted in endemic arsenic poisoning and fluorosis among the local residents (Bai et al., 2006; Luo, 2011; Zheng et al., 1999), implying the possibility of similar Hg poisoning.

Table 5
Statistical results of Hg^0 in the indoor atmosphere at 0.5 m above stone coal stove and fire pan in three families.

Family ID	Fuel type	Hg content ($\mu g \cdot kg^{-1}$)	Time (After fueling)	Hg^0 concentration ($ng \cdot m^{-3}$)		
				Min.	Max.	Mean ± SD
#2	Humic coal	14	0–6 min	1	162	20 ± 23
#8	Stone coal	1175	0–70 min	0	16,377	2023 ± 2526
			70–117 min	1	5472	431 ± 614
			117–195 min	0	450	73 ± 67
	Humic coal	21	0–12 min	0	394	60 ± 53
#9	Stone coal	632	0–18 min	3	22,691	2416 ± 3748
			180–192 min	4	416	67 ± 66

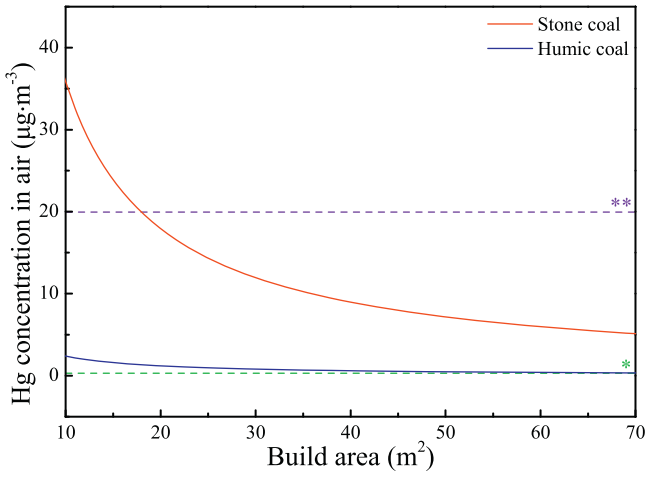

Fig. 5. Estimated gaseous elemental mercury in a closed indoor air burning stone/humic coal. *, 0.3 μg m^{-3}, the national standard for Hg in residential area (TJ36-1979) **, 20 μg m^{-3}, the national standard for Hg in workshop (GB 16227-1996).

3.3. Estimation of Hg emission from stone coal combustion

Mercury emission factors (MEF) of residential stove in southern Shaanxi province were estimated based on the mass balance method (Table 6). The above discussions suggest that nearly all (95.5–99.4%) Hg in the fuel will lost into ambient air during the residential combustion process. MEF can thus be estimated based on coal mass (MEF^{M}) and heat value (MEF^{HV}) according to Eqs. (3) and (4):

$$MEF^{M} = \frac{M_{Hg}}{M_{fuel}} \times MER_{Hg} = C_{fuel}^{Hg} \times MER_{Hg} \quad (3)$$

$$MEF^{HV} = \frac{\frac{M_{Hg}}{M_{fuel}} \times MER_{Hg}}{HV_{fuel}} = \frac{C_{fuel}^{Hg} \times MER_{Hg}}{HV_{fuel}} \quad (4)$$

where M_{Hg} and M_{fuel} are the mass of Hg (μg) and different kinds of fuels (kg) added into the stoves, respectively; MER_{Hg} is mercury emission ratio (%) as mentioned above; C_{fuel}^{Hg} is Hg concentration in different type of fuels (μg·kg^{-1}); and HV_{fuel} is the average heat value of different types of fuels (MJ·kg^{-1}).

MEF based on fuel mass is estimated to be in the range of 218.3–1172.5 (average 537.8) μg Hg·kg^{-1} for stone coal, 5.4–168.3 (average 35.8) μg Hg·kg^{-1} for humic coal, and 2.4–25.7 (average 14.0) μg Hg·kg^{-1} for charcoal (Table 6). Kim et al. (2010) estimated the emission factors of coal-fired power plants (CFPPs) before air pollution control devices(APCDs) to be 56.5 μg Hg·kg^{-1} coal for bituminous coal or 82.1 μg Hg·kg^{-1} coal for anthracite coal. Our research on 15 CFPPs in north China and southwest China showed that atmospheric Hg emissions from this source have been dramatically reduced in the recent 10 years, e.g., > 90% Hg in feed coal was retained in the fly ash and FGD gypsum, and the atmospheric Hg emission factor declined to 8 ± 10 μg Hg·kg^{-1} coal (range: 1–33 μg Hg·kg^{-1} coal, N = 15) (Tang et al., 2016; Li et al., 2019a,b; and unpublished data). Therefore, stone coal would release more than ten times higher Hg of residential humic coal and over 60 times higher than CFPPs based on the same amount of fuel. MEF based on heat value is estimated to be 62.6 μg Hg·MJ^{-1}, 1.51 μg Hg·MJ^{-1} and 0.50 μg Hg·MJ^{-1} for stone coal, humic coal and charcoal, respectively (Table 6), which means that, in order to produce the same amount of heat, stone coal released 40–120 times more Hg than humic coal and charcoal due to its low calorific value and high Hg content.

Table 6
Hg emission factors of different fuel types in this study.

Sample type	MEF^{M} (μg Hg·kg^{-1} fuel)			MEF^{HV} (μg Hg·MJ^{-1})		
	Min	Max	Mean	Min	Max	Mean
Humic coal (N = 14)	5.38	168.32	35.80	0.23	7.11	1.51
Stone coal (N = 10)	218.34	1171.45	537.77	25.41	136.32	62.58
Charcoal (N = 2)	2.37	25.68	14.03	0.08	0.92	0.50

Annual Hg emission from stone coal burning can also be estimated from MEF based on the stone coal mass:

$$Hg^{y} = M_{coal}^{y} \times MEF^{M} \quad (5)$$

where Hg^{y} and M_{coal}^{y} are annual Hg emissions and the amount of stone coal burnt, respectively.

In Shaanxi province, stone coal was mainly (> 90%) produced in Ankang with amounts of 0.6 Tg (10^{12}g) in 2004 and 2.5 Tg in 2011 (Liu et al., 2016; Wang, 2011). Combining the amount of stone coal consumed, the corresponding Hg content and the mercury emission ratio, about 1.34 ± 0.24 (range: 0.54–2.94) Mg Hg would have been emitted into the ambient air through the combustion of stone coal in Shaanxi province in 2011. There are abundant stone coal resources in southern China, and stone coal is also used in some industrial activities such as lime/cement production, brick making and utility CFB boilers (GRI-CSA, 1982; Dai et al., 2018). In Zhejiang province alone, 4 Tg of stone coal was produced in 2003 (Ye et al., 2004), while at the national scale, the total production of stone coal was not clear. Hence, stone coal, which has been neglected in the statistics of Hg emissions, is a potential atmospheric Hg source in China and deserve more attention in estimating total national atmospheric Hg emissions.

4. Conclusions

Stone coal is characterized with low moisture, volatility and heat value, and high contents of ash and Hg in southern Shaanxi province of China. This preliminary research showed that Hg emission factors of stone coal, whether based on mass (537.8 μg Hg·kg^{-1} coal) or heat value (62.6 μg Hg·MJ^{-1}), were much higher than those of humic coal and charcoal. Extremely high Hg concentrations above the stone coal stoves, e.g., up to 22,691 ng·m^{-3} (average 2416 ± 3748 ng·m^{-3}), could potentially cause health risks in non-ventilated rooms. Hg emissions from stone coal were estimated to be 1.34 Mg in Shaanxi province in 2011, but this emission source was not properly incorporated in the existing Hg emission statistical data. A more complete survey on stone coal usage and associated Hg content at the national scale, as well as the total and speciated Hg emissions from stone coal combustion and their isotopically compositions, are needed to improve the current Hg emission database in China and to understand the geochemistry of Hg in the environment. Human health related samples, such as indoor air Hg concentration, and hair/urine samples of the inhabitants, should also be collected and analyzed in regions where stone coal is used in order to assess the Hg burden to the inhabitants. A recommendation to the residential stone coal users is to replace stone coal with high heat value and low Hg fuels or other cleaner energy, and to improve ventilation in order to avoid Hg exposure risks.

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