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Domestic coal combustion can emit various air pollutants. In the present study, we measured emissions of particulate matter (PM) and gaseous pollutants from burning a specially formulated honeycomb coal (H-coal) and a coal cake (C-coal). Flue gas samples for PM_{2.5}, PM coarse (PM_{2.5–10}), and TSP were collected isokinetically using a cascade impactor; PM mass concentrations were determined gravimetrically. Concentrations of SO₂, NO_x, and ionic Cr(VI) in PM were analyzed using spectrometric methods. Fluoride concentrations were measured using a specific ion electrode method. PM elemental components were analyzed using an X-ray fluorescence technique. Total (gas and particle phase) benzo[a]pyrene (BaP) concentration was determined using an HPLC/fluorescence method. Elemental and organic carbon contents of PM were analyzed using a thermal/optical reflectance technique. The compositional and structural differences between the H-coal and C-coal resulted in different emission characteristics. In generating 1 MJ of delivered energy, the H-coal resulted in a significant reduction in emissions of

SO₂ (by 68%), NO_x (by 47%), and TSP (by 56%) as compared to the C-coal, whereas the emissions of PM_{2.5} and total BaP from the H-coal combustion were 2–3-fold higher, indicating that improvements are needed to further reduce emissions of these pollutants in developing future honeycomb coals. Although the H-coal and the C-coal had similar emission factors for gas-phase fluoride, the H-coal had a particle-phase fluoride emission factor that was only half that of the C-coal. The H-coal had lower energy-based emissions of all the measured toxic elements in TSP but higher emissions of Cd and Ni in PM_{2.5}.

Introduction

China has the largest coal production and consumption in the world (1). It has been estimated that more than 400 million people in China use coal for cooking and heating (2, 3). Due to the limited storage of petroleum and natural gas and relatively abundant coal storage (1000 billion ton) in China, it can be predicted that this coal-based energy structure in China may last for many years to come. Coal combustion, unfortunately, produces a wide variety of air pollutants including particulate matter (PM), carbon monoxide (CO), carbon dioxide (CO₂), sulfur dioxide (SO₂), nitrogen oxides (NO_x), and a large suite of organic toxics (4–8). The environmental and public health concerns over the coal emissions have motivated the coal research community to develop technologies that can reduce toxic emissions from coal combustion. One relatively inexpensive method is to burn coal in formulated form instead of burning raw coal, because formulation of raw coals can enhance coal combustion efficiency and reduce air pollution emission potentials (10, 11). Formulated coals are usually made in briquette form. Our previous research demonstrated that a formulated boiler briquette coal, compared to its raw coal precursor, substantially improved combustion efficiency when used in a traditional steam-generating boiler and reduced emissions of major air pollutants including PM_{2.5}, SO₂, CO, CO₂, and some toxic metals in PM (10, 11).

Honeycomb coal briquettes are usually used in household cooking/heating stoves. It is estimated that ~70 million ton of coal is consumed for domestic usage per year in China, of which 50 million ton is in the form of honeycomb coal. Honeycomb coal briquettes are developed historically from a standpoint of ease in use (transportation, handling, storage, and burning). Reducing toxic emissions has not necessarily been considered by numerous local “manufacturers” across China. In attempts to improve combustion efficiency and to reduce toxic emissions, scientists from the Institute of Coal Chemistry of the Chinese Academy of Sciences have formulated a new honeycomb coal (H-coal) designed for household use. The objective of this study is to characterize the emissions from combustion of the newly formulated H-coal. For comparison, the emissions from combustion of a coal cake (C-coal), which was made from the same raw coal as was for the H-coal, were also characterized. We determined the concentrations, emission rates, and emission factors of PM, SO₂, NO_x, benzo[a]pyrene (BaP), fluoride (F[–]), and toxic elements in PM for the H-coal and the C-coal. The elemental source profile of the emitted PM was also characterized for both coals.

Materials and Methods

Tested Coals. The raw coal used to formulate H-coal and C-coal was from a mine located in Yangquan, Shanxi

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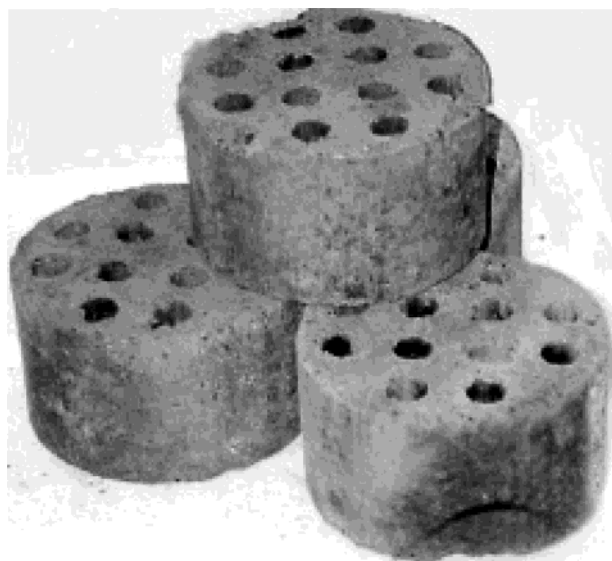


FIGURE 1. Honeycomb coal.

TABLE 1. Proximate and Ultimate Analysis for the Coals Tested^a

	H-coal	C-coal	R-coal ^b	typical Chinese H-coals ^c
Proximate Analysis				
ash	33.85	30.21	13.58	25.4–49.3
moisture	1.67	2.85	2.05	1.80–4.39
volatile matter	12.28	11.27	8.17	5.15–11.9
fixed carbon	52.2	55.67	76.2	41.4–56.7
Ultimate Analysis				
carbon	56.09	62.3	78.22	54.3–63.6
hydrogen	2.99	2.64	2.7	0.28–2.6
oxygen	3.43	2.76	0.76	
nitrogen	0.66	0.83	0.73	
sulfur	1.31	1.58	1.96	0.17–0.94

^a All contents are in percent (%) by weight on a dry fuel basis. ^b The raw coal from which the H-coal and the C-coal were made. ^c Ref 9.

Province. The raw coal contained powders smaller than 13 mm (accounting for about 30 wt %) and coal pieces with a diameter ranging from 13 to 25 mm. The H-coal formulation is patented (Chinese Patent No. ZL 97 1 20946.4; International Patent No. C10L5/04) and is briefly described as follows.

After being pulverized into coal powders, the raw coal is mixed with hydrate lime ($\text{Ca}(\text{OH})_2$, 15%), a combustion-promoting agent (0.5%), a waterproofing agent (0.03%), and a binding agent (11.5%). The mixture is then pressed into a cylinder 110 mm in diameter and 90 mm high, with 10 holes from top to bottom (Figure 1). Each H-coal weighs about 1500 g and can burn for ~60 min, depending on the air supply. To fit the household stoves used in the study, the raw coal was shaped into coal cake (C-coal) by mixing raw coal (80%) with clay (20%) as binding material. The C-coal weighed 400 g and can burn for 20 min. The H-coal, the C-coal, and the raw coal from which the H-coal and the C-coal were made were characterized by proximate and ultimate analysis performed by the Institute of Coal Chemistry (Table 1). For comparison, the range of the composition of other Chinese honeycomb coals is also summarized in Table 1.

Test Stove. The stove chosen for the study was one of those most widely used to burn honeycomb coal briquettes and coal cakes in China. In winter months, this type of stove is usually used for both cooking and heating. The experimental setup is shown schematically in Figure 2. Coals were loaded from the top of the stove into the burning chamber, and the ash fell down into the bottom chamber of the stove. The bottom chamber of the stove was separated from the burning chamber for ash storage. An ash door was used to control the air supply flow and thus the heat output (power). The ash door is usually closed when the stove is not in use and is usually open to provide more oxygen when the stove is used for cooking and heating. The H-coal had a substantially improved thermal efficiency versus the C-coal (35% vs 23%, see Table 2), as a result of the special H-coal formulation (e.g., adding combustion-promoting agent, more uniform combustion in the stove combustion chamber). Each stove was equipped with a flue, as shown in Figure 2. The majority of the coal-emitted gas was exhausted through the flue connected to the stoves. Coal combustion in cook stove is not a steady-state process. An integrated sampling approach was used to collect air pollutant emissions during an entire burn cycle (from fire start to fire extinction) as described in the following sections. This approach provides emission data that can represent a realistic burning situation (8).

PM Sampling. A sampling probe was placed at the center of the flue of the stove, facing the direction of the chimney gas flow. As shown in Figure 2, the height of sampling port was 2 m above ground level. The sampling point is 0.9 m

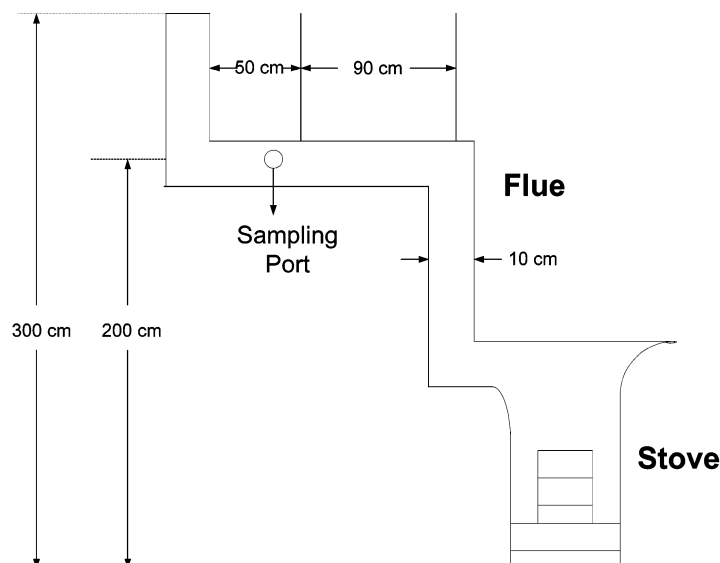


FIGURE 2. Schematic of sampling platform for household stove fueled with honeycomb and briquettes. The stove was a cylinder 24 cm in diameter and 50 cm in height. The burning chamber inside the stove was 30 cm in height and 12 cm in diameter.

TABLE 2. Operating Conditions of the Test Stove Using H-Coal and C-Coal^a

parameter	unit	H-coal	C-coal
fuel burn rate	kg/h	1.49 (0.07)	1.2 (0.09)
flue gas temperature	°C	183 (7)	155 (4)
flue gas humidity	%	3.13 (0.5)	4.03 (0.4)
flue gas velocity	m/s	0.95 (0.05)	0.8 (0.05)
flue gas emission rate	m ³ /h	15.7 (1.5)	13.8 (1.4)
flue gas emission factor ^b	m ³ /kg	10.46	11.51
flue gross heat value	MJ/kg	21.92 (0.12)	23.26 (0.23)
delivered heat value	MJ/kg	7.67 (0.61)	5.42 (0.22)
stove thermal efficiency ^b	%	35	23

^a Standard deviations ($n = 3$) in parentheses. ^b Calculated average value.

away from the stove. The flue gas was drawn through the sampling probe under isokinetic conditions and diluted in a previously described dilution system (10). During the dilution process, the flue gas was cooled to ambient temperature. PM was collected and segregated by particle size using a PM_{2.5}/PM₁₀/TSP cascade impactor. The impactor was operated at a flow rate of 36 L/min to maintain the aerodynamic cut-point for each stage. The particles were collected on glass-fiber filters (Whatman 934AH, Clifton, NJ). Another set of PM_{2.5} and PM₁₀ samples were also collected for elemental and organic carbon analysis based on the sampling system and method reported by Ge et al. (10).

Three replicated measurements of the size-resolved particles were acquired for both raw coal and coal cake. Field and laboratory blanks were used to allow evaluation of potential contamination of blank filters and samples during preparation, weighing, storage, sampling, transportation, and laboratory analyses. All the filter samples and blanks were placed in clean Petri dishes individually during transportation in coolers and storage in freezers.

Analysis of PM Samples. Prior to and following sampling, the filters were weighed using an electronic microbalance with a sensitivity of 1 μ g. A ²¹⁰Po radioactive source was used to remove static charge during filter weighing. Before weighing, all filters were conditioned for at least 24 h in a temperature- (20 ± 2.0 °C) and relative humidity-controlled ($40 \pm 5\%$) environment at the Research Institute of Physical & Chemical Engineering of Nuclear Industry (Tian Jin, China). The mass concentrations of PM_{2.5} and PM₁₀ were determined using the net weight increases of the sample filters and the sampling volumes.

After the gravimetric analysis, the filters were analyzed for 40 elements using an X-ray fluorescence (XRF) spectrometer at Desert Research Institute (DRI) in Reno, NV (12). Vacuum deposit thin-film standards were used as calibration standards, and polymer films were used as quality control standards. Blank filters from the same manufacturing lot as the sample filters were analyzed along with the PM sample filters. An average blank spectrum was constructed and used for spectral background subtraction of the exposed filters.

The collected samples were then submitted for hexavalent chromium [Cr(VI)] using a visible absorption spectrophotometric method, which was modified from NIOSH standard method 7600 (14). The filter was placed in a 50-mL beaker containing 5 mL of 2% NaOH/3% Na₂CO₃. The beaker was covered with a watch glass and heated to near the boiling point for 30 min. During the extraction process, the headspace above the solution was purged with nitrogen to avoid oxidation of Cr(III) in the sample. The resolution was cooled to room temperature and mixed with 1.9 mL of 6 N sulfuric acid and 0.5 mL of 2.5 mg/mL diphenylcarbazide in water/acetone (1:1). The resulting solution was diluted to 25 mL with distilled water and analyzed with a spectrophotometer at a wavelength of 540 nm. Before analysis, all samples were

stored in a freezer (-20 °C) and analyzed for Cr(VI) within 2 weeks. The detection limit of this method was 1.0 μ g/g.

The separate set of PM_{2.5} and PM₁₀ samples that were collected on quartz-fiber filter substrates were analyzed for organic carbon (OC) and elemental carbon (EC) using the thermal/optical reflectance (TOR) carbon analyzer at DRI (Reno, NV). The TOR method and quality control details were described by Chow et al. (13).

Collection and Analysis of SO₂ and NO_x in Flue Gas. The SO₂ emission was collected and analyzed following the Chinese State Environmental Protection Administration's (SEPA) standard method, which is similar to the U.S. EPA's standard method and described in Zhang et al. (11). Triplicate samples of flue gas were collected using an impinger with a solution of formaldehyde, potassium biphthalate, and Na₂-CDTA. SO₂ was then determined colorimetrically at a wavelength of 575 nm.

The concentrations of NO_x were measured using a method adapted from the NIOSH standard method 6014 (14). Flue gas was collected at a flow rate of 0.3 L/min. An inline chromat filter was used to oxidize nitric oxide (NO) to NO₂. The total nitrogen dioxide was then collected in an impinger containing a triethanolamine solution. The NO₂ concentration was determined by a spectrophotometer at a wavelength of 540 nm after addition of hydrogen peroxide, sulfanilamide, and *N*-(1-naphthyl)ethylenediamine dihydrochloride (NEDA) solutions. The detection limit of the method was 2.0 mg/m³. A calibration curve was prepared daily with NaNO₂ solution ranging from 0.1 to 20 μ g/mL.

Collection and Analysis of Fluoride in Flue Gas. Fluoride (F⁻) in flue gas was sampled and analyzed using a standard method certified by SEPA (16). Three citric acid-impregnated cellulose ester membrane filters followed by a potassium dihydrogen phosphate-soaked cellulose ester membrane filter (with pad) were used to collect F⁻ in PM_{2.5}, PM_{2.5-10}, TSP-PM₁₀, and gas-phase F⁻, respectively. The PM_{2.5}/PM₁₀/TSP separator was used to separate the PM by size. The sample was drawn from the flue gas isokinetically at a flow rate of 36 L/min. Particulate fluorides were fused in sodium hydroxide and then dissolved in 10 mL of water and total ionic strength activity buffer (TISAB). The pH of the buffer was ~ 5 , a level at which F⁻ was the predominant fluorine-containing species. The buffer contained cyclohexylene-dinitrilotetraacetic acid, which formed stable complexes with Fe(III) and Al(III), thus removing interferences by freeing fluoride ions from complexes with these ions (14). Gaseous fluorides were extracted with 10 mL of water and TISAB. The extracts were then analyzed using ion-selective electrode method. Sodium fluoride was used to prepare the calibration curve. The method detection limit was 4 μ g/m³.

Collection and Analysis of BaP in Flue Gas. Total BaP, including both gas- and particle-phase BaP was collected and analyzed. The sampling probe nozzle was connected with a stainless steel sampling tube where the majority of gas-phase BaP was condensed into particulate phase. The sampling tube was equipped with a water jacket through which tap water flew to keep the temperature of the sampling tube lower than 40 °C. This design was to prevent possible reactions between PAHs in the gas phase and NO_x at high temperature (17). The particle-phase BaP was collected on a glass-fiber filter using an air-sampling pump at a flow rate of 12.5 L/min. An impinger containing 50 mL of cyclohexane was placed between the glass-fiber filter and the pump to capture the remaining vapor-phase BaP. Prior to sampling, all parts of the sampling train were cleaned and rinsed with anhydrous ethanol twice. This method was validated and comparable to BaP measured using the U.S. EPA proposed Modified Method 5, which is typically used for semivolatile organic material sampling (18).

TABLE 3. Concentrations (mg/m³) and Size Distributions of Particles Emitted from Burning of H-Coal and C-Coal

diameter (μm)	H-coal				C-coal			
	mean	SD	N	% of TSP	mean	SD	N	% of TSP
PM _{2.5}	38.4	3.8	3	65.4	8.5	4.3	3	9.8
PM _{2.5-10}	10.2	6.6	3	17.3	18.9	8.7	3	21.8
PM ₁₀	48.6	5.4	3	82.6	27.4	7.6	3	31.6
TSP-PM ₁₀	10.2	5.9	3	17.4	59.1	9.2	3	68.4
TSP	58.8	2.4	3	100.0	86.5	5.3	3	100.0

After sampling, the probe nozzle and the sampling tube were rinsed with 20 mL of doubly distilled cyclohexane for 5 times to recover BaP residuals condensed onto the sampling parts. The cyclohexane extracts were combined with 50 mL of cyclohexane for collection of vapor-phase BaP and stored in a glass bottle. The glass-fiber filter was wrapped with aluminum foil and stored at -20 °C for up to 1 week prior to extraction with 50 mL of cyclohexane for 16 h at 98 °C using a Soxhlet apparatus (19, 20). The cyclohexane extracts were combined, evaporated to near dryness, and reconstituted in 1 mL of acetonitrile (ACN). The extracts were analyzed using an (HPLC) system (model 638-50; Hitachi Co. Ltd, Tokyo, Japan) with a fluorescence detector (RF-510, Shimadzu, Kyoto, Japan). The HPLC column used was an Supelcosil LC-PAH column (4.6 × 250 mm) (Supleco Inc., Bellefonte, PA) under controlled temperature at 30 °C. The chromatographic separation was performed under isocratic conditions (methanol:water = 90:10). The mobile phase flow rate was 1 mL min⁻¹. The injection volume was 10 μL. The fluorescence detector was set at an excitation wavelength of 360 nm and an emission wavelength of 440 nm. BaP concentrations were quantified through a calibration curve prepared using external standards.

Determination of Emission Rates and Emission Factors.

Emission rates (mg/h) of the measured pollutants were calculated by multiplying the flue gas concentrations (mg/m³) and the flue gas emission rate (m³/h). Mass-based emission factors (mg/kg of coal) were obtained by dividing the emission rates (mg/h) with the fuel burn rates (kg/h). The energy-based emission factors (mg/MJ) were derived from mass-based emission factors and delivered heat values (MJ/kg).

Results

Concentrations of Air Pollutants in Flue Gas. The particle concentrations and size distributions are listed in Table 3. Although TSP concentration resulting from combustion of the H-coal briquette was about two-thirds that from the C-coal, the PM_{2.5} concentration for the H-coal was 4–5 times higher. Approximately 65% and 83% of TSP from the H-coal were PM_{2.5} and PM₁₀, respectively, compared to 10% and 32% for the C-coal. Both the H-coal (17%) and the C-coal (22%) produced similar portions of PM coarse (PM_{2.5-10}). The concentrations of PM_{2.5} and PM₁₀ collected using the cascade impactor were comparable to those using single-stage impactors. On the basis of the results from the single-stage impactors, the PM_{2.5} concentrations were 37.6 ± 2.7 and 7.4 ± 1.5 mg/m³, respectively, and the PM₁₀ concentrations were 51.5 ± 6.1 and 23.9 ± 9.1 mg/m³, respectively, for the H-coal and the C-coal.

The concentrations of SO₂, NO_x, F⁻ (gas), and B(a)P are shown in Table 4. While NO_x emissions were similar, the SO₂ concentration emitted from burning the H-coal was nearly half of those from the C-coal. An order of magnitude higher B(a)P concentration was observed during the H-coal burning however.

OC and EC Contents of PM_{2.5} and PM₁₀. The EC contents in PM were 3.9%/0.66% (PM_{2.5}/PM₁₀) and 0.47%/0.24%

TABLE 4. Concentrations of Air Pollutants in Flue Gas (mg/m³) during Burning of H-Coal and C-Coal

compound	H-coal			C-coal		
	mean	SD	N	mean	SD	N
SO ₂	431.5	196.0	3	862.0	246.0	3
NO _x	6.7	1.4	3	8.2	1.0	3
fluoride (gas-phase)	0.5	0.3	3	0.3	0.1	3
BaP	1.0E-03	8.9E-04	7	1.8E-04	1.9E-04	7

(PM_{2.5}/PM₁₀) for the C-coal and the H-coal, respectively. The OC contents in PM were 11.9%/7.3% (PM_{2.5}/PM₁₀) and 2.5%/4.0% (PM_{2.5}/PM₁₀) for the C-coal and the H-coal, respectively. The lower carbon contents of the PM_{2.5} and PM₁₀ emitted from the H-coal combustion might result from the lower carbon content of the H-coal (Table 1) and higher combustion efficiency. EC abundances are 2–6 times higher for C-coal as compared to H-coal, suggesting incomplete combustion in C-coal.

PM Elemental Profile and Toxic Trace Elements. Source profile data are important for source apportioning analysis. The PM concentrations of five toxic trace elements and two toxic ions (F⁻ and Cr(VI)) are reported in Table 5. All these toxic elements are included in the U.S. EPA hazardous air pollutants (HAPs) list (21). All the measured air toxics concentrations were higher in both PM_{2.5} and PM₁₀ but lower in particles larger than 10 μm in the C-coal emission. Lead (Pb) and F⁻ were the most abundant elements with concentrations 1 or 2 orders of magnitude higher than the other elements in particles. PM_{2.5} arsenic (As), F⁻, and Cr(VI) were also abundant elements in the C-coal, with concentrations exceeding 1000 μg/g. However, in the H-coal PM_{2.5} and PM₁₀, only Pb and F⁻ had concentrations exceeding 1000 μg/g.

The concentrations of the other elements in PM_{2.5} and PM₁₀ are reported in Table 6. Of those elements, Se, As, Cr, Co, Cu, and Al are characteristic elements for emissions from coal combustion. Except for Cu, the other five elements were present at higher concentrations in the PM_{2.5} and PM₁₀ emitted from the C-coal combustion.

Discussion

Sulfur dioxide is a major air pollutant in China. Epidemiological studies in China have demonstrated that exposure to SO₂ is significantly associated with increased morbidity and population risks of cardiovascular and respiratory mortality (22, 23). In 1998, the annual average SO₂ concentrations in ambient air were found to be higher than 120 μg/m³ in about 50 Chinese cities, as a consequence of burning untreated raw coal with high sulfur content (11). Therefore, the primary objective of the development of the H-coal was to reduce the SO₂ emission. In the present study, 15% of Ca(OH)₂ was added to the H-coal to capture the emitted SO₂ at high temperature (950–1100 °C) during the coal burning process. The produced CaSO₄ is fixed in the combustion slag and ash (24). In addition, due to the addition of the combustion-promoting agent, waterproofing agent, binding agent, and sulfur fixation agent (Ca(OH)₂), the sulfur content of the H-coal (1.31%) was lower than that of the C-coal (1.58%) (Table 1). The transformation of raw coal to the H-coal resulted in a significant SO₂ emission reduction as expected. The emission rate and mass-based emission factor of SO₂ for the H-coal were only about half of those for the untreated C-coal (Table 7). Furthermore, in generating 1 MJ of delivered heat, the H-coal emitted less than one-third of SO₂ from the C-coal. Therefore, the use of the H-coal would substantially reduce the SO₂ emissions, even after taking account of the difference in sulfur content between H-coal and C-coal.

Particulate air pollution is a serious environmental and public health concern in developing countries. In China,

TABLE 5. Toxic Elements in Particles Generated from Burning H-Coal and C-Coal^a

element	H-coal						C-coal					
	in PM _{2.5}		in PM ₁₀		in TSP-PM ₁₀		in PM _{2.5}		in PM ₁₀		in TSP-PM ₁₀	
	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD
As	224	107	590	58	750	47	2 370	1 680	2 050	710	720	6
Cd	174	79	142	71	90	2.7	313	30	302	54	5	0.01
Ni	283	144	466	320	3 170	30	730	678	659	300	380	30
Pb	5 120	570	5 900	2 080	2 550	30	29 900	10 100	25 500	4 300	1 650	40
F ⁻	2 990	1 660	2 580	180	557	30	4 420	4 310	3 940	3 670	1 050	100
Cr	253	231	434	400	4150	20	1 210	1 650	365	60	640	2
Cr(VI)	118	10	106	10	490	40	379	40	226	20	84.6	8

^a Unit in $\mu\text{g/g}$ of PM.TABLE 6. Elemental Concentrations in PM_{2.5} and PM₁₀ Resulting from Burning H-Coal and C-Coal^a

element	H-coal				C-coal			
	in PM _{2.5}		in PM ₁₀		in PM _{2.5}		in PM ₁₀	
	mean	SD	mean	SD	mean	SD	mean	SD
Na	127 000	53 300	150 000	34 200	bdl	bdl	2 400	4 170
Mg	bdl	bdl	bdl	bdl	2 960	2 780	1 480	2 560
Al	1 320	1 870	332	77	14 700	3 350	1 570	611
Si	3 490	1 850	947	865	33 900	12 100	3 940	1 090
P	bdl	bdl	bdl	bdl	816	725	394	565
S	302 000	84 200	128 000	41 800	367 000	80 600	126 000	27 700
Cl	105 000	149 000	126 000	169 000	bdl	bdl	49 200	85 300
K	174 000	31 200	130 000	13 400	11 900	847	5 410	4 130
Ca	562	152	472	258	5 760	3 470	1 480	223
Ti	bdl	bdl	bdl	bdl	628	550	bdl	bdl
V	1	2	bdl	bdl	bdl	bdl	bdl	bdl
Mn	31	18	5	2	29	35	19	32
Fe	781	18	782	337	7 770	4 100	1 840	410
Co	11	1	13	2	31	29	64	53
Cu	279	27	255	52	79	87	75	128
Zn	2 700	1 260	7 450	4 870	46 200	11 400	30 900	36 300
Ga	76	108	67	29	901	584	519	808
Se	259	32	315	95	2 190	678	1 620	1 260
Br	763	1 050	1 540	1 840	261	452	4 160	7 200
Rb	1 030	80	989	61	98	24	39	9
Sr	1	1	bdl	bdl	80	125	bdl	bdl
Yt	6	9	bdl	bdl	bdl	bdl	7	12
Zr	12	14	23	2	147	57	37	40
Mo	76	20	58	20	96	85	bdl	1
Nd	49	70	65	74	471	233	190	330
Ag	bdl	bdl	36	51	384	642	bdl	bdl
In	59	65	44	62	714	761	130	115
Sn	214	58	450	112	3 510	876	2 060	1 470
Sb	122	172	54	76	363	504	730	64
Ba	498	218	457	34	1 190	2 070	593	587
La	582	178	272	384	2 360	3 360	1 840	1 650
Au	47	66	62	4	431	415	196	340
Tl	13	6	bdl	bdl	106	96	99	88
Ur	16	22	bdl	bdl	bdl	bdl	31	50

^a Unit in $\mu\text{g/g}$ of PM. bdl, below detection limitation.

approximately one million premature deaths are thought to be attributable to particulate air pollution every year (1). The use of coal and other solid fuels for residential cooking and heating is a primary source of the indoor and outdoor particulate air pollution (15, 25–27). Since there are still high TSP levels in many outdoor and indoor environments in China ($> 200 \mu\text{g}/\text{m}^3$), monitoring ambient TSP is still an active regulation requirement in China (26, 28). In 1996, SEPA issued a revision of the ambient air quality standard (GB 3095–1996) that requires daily or weekly monitoring of PM₁₀ concentrations in major urban cities. We included measurement of PM₁₀ and PM_{2.5} emissions in this study, although SEPA has not included PM_{2.5} in the current air quality standards. However, exposures to fine PM (PM_{2.5}) have been associated with various health outcomes including mortality, respiratory morbidity, and cardiovascular morbidity (29).

The emission rate, mass-, and energy-based emission factors of TSP for the H-coal were lower than the corresponding values calculated for the C-coal. As shown in Table

7, the energy-based emission factor of TSP for H-coal and C-coal were 80.1 and 183.6 mg/MJ, respectively. Therefore, in generating 1 MJ of delivered energy, using the H-coal in place of the C-coal would lead to a 56.4% reduction in TSP emission. A recent study reported that combustion of different honeycomb coals in Chinese household stoves could produce 50–80 mg TSP in generating 1 MJ of delivered energy (8). These values are comparable to that for the H-coal used in the present study. The combustion of the H-coal in the household stove generated comparable PM₁₀ to the C-coal in terms of generating the same amount of delivered energy (Table 7). However, the H-coal PM_{2.5} emission factor (energy-based) was nearly 3 times that of the C-coal (Table 7). In contrast, combustion of the C-coal produced a greater amount of coarse particles (PM_{2.5–10} and TSP-PM₁₀) and thus led to a higher TSP emission factor. This finding suggests that reduction of PM_{2.5} be considered in future modification of the H-coal and for developing other new types of formulated coals.

TABLE 7. Emission Rates and Emission Factors of Measured Pollutants for H-Coal and C-Coal^a

pollutant	emission rate (mg/h)				emission factor (mass-based, mg/kg)				emission factor (energy-based, mg/MJ)			
	H-coal		C-coal		H-coal		C-coal		H-coal		C-coal	
	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD
PM _{2.5}	603	59.1	117	58.7	401	39.4	97.8	49.0	52.4	5.1	18.1	9.0
PM _{2.5-10}	159	102	260	119	106	68.6	217	99.9	13.8	8.9	40.0	18.4
PM ₁₀	762	84.2	377	104	507	56.1	314	87.1	66.2	7.3	58.1	16.1
TSP-PM ₁₀	160	92.1	815	127	106	61.4	680	106	13.9	8.0	125	19.6
TSP	922	37.2	1190	73.0	614	24.8	995	60.9	80.1	3.2	183	11.2
SO ₂	6770	3080	11900	3390	4510	2050	9920	2830	588	267	1830	522
NO _x	105	21.7	113.0	14.1	70.2	14.4	94.3	11.7	9.1	1.9	17.4	2.2
fluoride (gas)	8.3	4.9	4.8	1.1	5.5	3.2	4.0	1.0	0.7	0.4	0.7	0.2
BaP	1.6E-02	1.4E-02	2.5E-03	2.6E-03	1.1E-02	9.3E-03	2.1E-03	2.2E-03	1.4E-03	1.2E-03	3.9E-04	4.0E-04

^a A deterministic approach was used to determine average emission rates and factors. The standard deviations in the table only account for the marginal uncertainty in concentrations listed Tables 3–5 since larger variability in pollutant concentrations was observed than in parameters listed in Table 2. A Monte Carlo approach may be helpful for estimating the propagation of uncertainties in all parameters provided distributions of these parameters are well-identified in future studies.

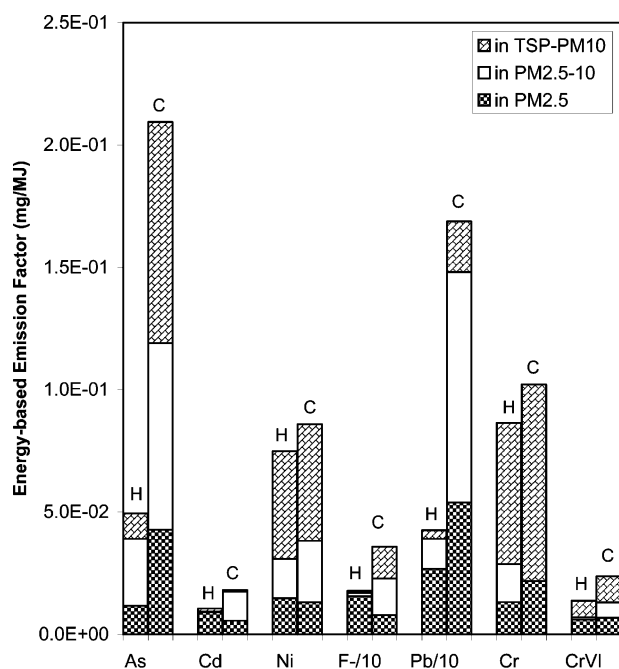


FIGURE 3. Emissions of measured toxic elements, in three PM size fractions, from burning the H-coal and C-coal. (H, H-coal; C, C-coal; the scale for F⁻ and Pb is 1 order of magnitude higher than shown).

NO_x are responsible for numerous environmental problems including photochemical smog, acid rain, water quality deterioration, global warming, visibility impairment, etc. (30). In addition, NO_x can react with atmospheric organic chemicals to produce various air toxics including nitroarenes and nitrosamines. As shown in Table 7, the emission rate of NO_x for the H-coal was slightly lower than that for the C-coal. On a fuel-mass basis, the H-coal produced an emission factor about 26% smaller than the C-coal. However, in generating the same amount of delivered energy, the H-coal produced only about half the amount of NO_x that the C-coal produced.

In China, more than 30 million people have suffered from dental and skeletal fluorosis due to exposure to fluoride compounds emitted from coal combustion (31, 32). Coal combustion produces both gas- and particulate-phase fluoride. By comparing the energy-based emission factors of gas-phase and particulate fluoride for the tested coals (Table 7 and Figure 3), we found that 80% and 66% of fluoride emitted from the H-coal and C-coal, respectively, were present in the gas phase, with similar concentration levels in generating 1 MJ of energy (Table 7). Total particulate-phase fluoride emitted per MJ of delivered energy by the H-coal was about

half that emitted by the C-coal. However, fluoride in PM_{2.5} emitted per 1 MJ delivered energy by the H-coal was about two times that emitted by the C-coal (Figure 3). At the present time, relative importances of fluoride in gas phase versus particulate phase and in coarse versus fine particles are unknown. Recent studies have shown that, besides direct inhalation exposure to coal-released airborne fluoride, ingestion of fluoride contaminated food due to deposition of airborne fluoride was also a significant exposure route for people who use coals for heating and cooking (33, 34). Therefore, fluoride emitted in gas phase, in fine particles, and in coarse particles may have different implications as to which exposure route(s) is important.

Incomplete combustion of coal can produce a large number of polycyclic aromatic hydrocarbons (PAHs). High airborne PAH indoor concentrations resulting from household coal combustion has been associated with elevated incidence of lung cancer in some regions of China (35, 36). The fuel-weight based emission factor of BaP was 11 μg/kg for the H-coal combustion and 2 μg/kg for the C-coal combustion. These values are at least 2–3 orders of magnitude lower than the BaP emission factor for wood burning in the United States (2–3 mg/kg) (37). The energy-based emission factor for the H-coal was also approximately 3 times that of the C-coal. A recent study (38) indicated that the PAH emissions were positively correlated with the volatile content of a fuel, possibly a consequence of incomplete combustion for a fuel with high volatile content, such as wood (39). The H-coal had a higher volatile content (12.3%) than the C-coal (11.3%). This might be a reason for the higher BaP emission factor for the H-coal. However, PAH formation is a complex process that can be affected by many factors including the organic content of a fuel, combustion temperature, oxygen supplying rate during combustion, and the structures of stoves, etc.

Toxic trace metals in PM can exacerbate health damage. The emission factors of the selected trace metals on a basis of delivered energy are plotted in Figure 3. For all particle size ranges, the Pb emissions from the H-coal and the C-coal appear to be at least 1 or 2 orders of magnitude higher than the emissions from the other metals. As shown in Figure 3, the emission factors of all the metals in TSP are higher for the C-coal than for the H-coal. The reduction resulting from using the H-coal in place of the C-coal are 76% for As, 41% for Cd, 13% for Ni, 75% for Pb, and 15% for Cr. PM_{2.5} emission factors for As, Pb, and Cr were lower but Cd and Ni were higher for the H-coal. Figure 3 shows that the vast majority of the Cd, Pb, and F⁻ were associated with PM₁₀.

The emission factors of both PM_{2.5} As and PM_{coarse} As were several times lower for the H-coal than for the C-coal. One of the additives in the H-coal was hydrated lime (Ca(OH)₂), which was primarily designed to capture SO₂ emissions.

Recent studies have shown that lime and hydrated lime can capture arsenic oxide from coal combustion and produce $\text{Ca}_3\text{As}_2\text{O}_8$ and $\text{Ca}_2\text{As}_2\text{O}_7$, which have higher boiling points than As_4O_6 and tend to be left in the combustion slag and ash (40, 41). This may explain the orders of magnitude lower emissions of As from the H-coal. Due to the linkage between arsenic compounds and harmful toxicological effects, reduction of arsenic emission from coal burning is of importance, especially in some regions of China where arsenic poisoning occurs because of the domestic use of the coal with high arsenic content (as summarized in ref 2).

Chromium has three most common forms: metallic chromium [Cr(0)], trivalent chromium [Cr(III)], and hexavalent chromium [Cr(VI)]. Metallic chromium does not occur naturally. Trivalent chromium naturally occurs in rocks, soil, plants, and animals, etc. When Cr(III)-containing materials are heated (including coal burning process), Cr(III) is oxidized to Cr(VI), which is the most toxic form and has been found to cause a wide variety of adverse health effects including carcinogenic effects in humans (42). For this reason, the present study attempted to measure Cr(VI) in addition to the measurements of Cr element in all forms. The energy-based emission factor of $\text{PM}_{2.5}$ -bound Cr(VI) was slightly lower for the H-coal than for the C-coal, while the energy-based emission factor of TSP-bound Cr(VI) for the H-coal was only half the value for the C-coal (Figure 3). By comparing the concentrations of total Cr and Cr(VI) in $\text{PM}_{2.5}$ bound (Table 5), we found that 47% and 31% of the total Cr was in the form of Cr(VI) for the H-coal and C-coal emissions, respectively. Finally, we want to state that the present study used only one formulation of H-coal and C-coal from one region. Hence, the generalization of the findings from the present study should be extremely careful without a systematic evaluation of representative samples of other types of honeycomb coal and coal cakes made in other regions of China.

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