

Primary PM_{2.5} and trace gas emissions from residential coal combustion: assessing semi-coke briquette for emission reduction in the Beijing-Tianjin-Hebei region, China



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ABSTRACT

In response to severe haze pollution, the Chinese State Council set PM_{2.5} improvement targets for the Beijing-Tianjin-Hebei (BTH) region in 2013. To achieve the targets for the residential sector, semi-coke briquettes are being considered as a replacement for traditional raw coals with the help of financial subsidy, but information on the emission from them and the impacts on the air quality is limited. Laboratory experiments were conducted to determine emission factors (EFs) for a typical semi-coke briquette, its parent material (bituminous raw-coal-chunk) and three types of traditional coals (bituminous raw-coal-chunk, anthracite raw-coal-chunk and anthracite coal-briquette) extensively used in BTH. Compared with the parent material, significant lower EFs of primary PM_{2.5}, organic carbon (OC), element carbon (EC), the sum of 16 polycyclic aromatic hydrocarbon components (PAHs), SO₄²⁻, NO₃⁻, hazardous trace elements (HTEs) and NO_x were found in semi-coke briquette. A scenario for the BTH region in 2015 in which raw coals were replaced with the semi-coke briquette showed that amounts of pollutants emitted from residential coal combustion could decrease by 91.6% for primary PM_{2.5}, 94.0% for OC, 99.6% for EC, 99.9% for PAHs, 94.2% for NO₃⁻, 45.6% for HTEs, 70.9% for NO_x and 22.3% for SO₂. However, SO₄²⁻ loadings evidently would increase if raw coals were replaced with either semi-coke briquette or anthracite coal-briquette. Geographic distributions of modeled reductions were developed to identify emission-reducing hot-spots and aid in the development of clean energy policies. Replacement of traditional raw coals with the semi-coke briquette apparently could lead to significant environmental improvements in BTH and other regions in China.

1. Introduction

China has been experiencing severe haze pollution, especially in winter when coal is used extensively for residential heating (Yan et al., 2017). Indeed, coal combustion is a major emission source of gases and fine particulate matter (PM, usually measured as PM_{2.5}, particles with aerodynamic diameters $\leq 2.5 \mu\text{m}$). Emissions from coal combustion have led to severe indoor and outdoor air pollution, and they have

become a serious national concern due to their adverse effects on health, visibility and the environment over regional and global scales (Huang et al., 2014; Li et al., 2017; Watson, 2002; Zheng et al., 2015).

The Beijing-Tianjin-Hebei (BTH) region is an important city agglomeration in China, where coal is still the primary fuel for residences in both urban and rural areas. In 2015, 20.5 Mt of raw coals were burned in BTH for residential uses, and that amounted to 20.3% of the total residential coal consumption in China (Fig. 1). Residential coal

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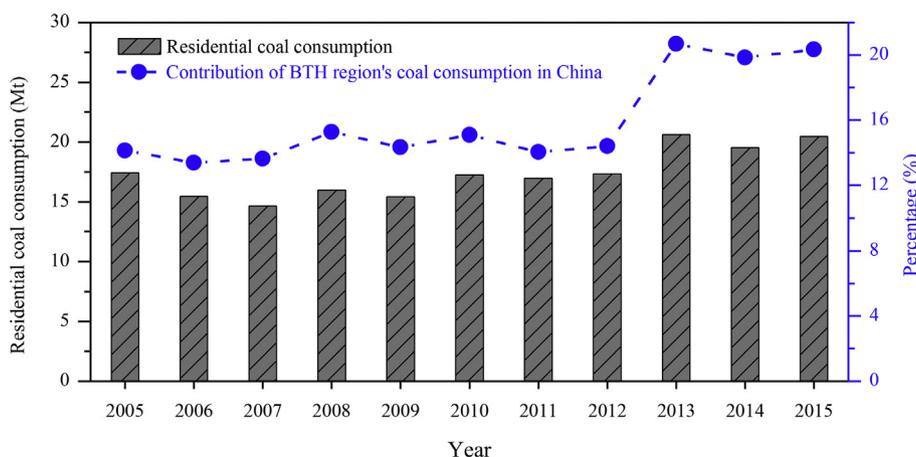


Fig. 1. Residential coal consumption in the Beijing-Tianjin-Hebei (BTH) region and the percentage of coal consumption in BTH out of the total household coal consumption in China. Source: China Energy Statistical Yearbook (2006–2016).

combustion is a major contributor to severe haze pollution in winter in this region. For instance, Zhang et al. (2017) reported that residential coal combustion contributed 46% of the monthly average $PM_{2.5}$ concentrations during BTH haze episodes in 2015 using WRF-CMAQ model. In response to the serious haze pollution events, the Chinese State Council released the National Air Pollution Prevention and Control Action Plan (2013–2017) in 2013 aiming to reduce $PM_{2.5}$ loadings. The policies were designed to cut down coal consumption and replace low rank coals (bituminous coals) with clean fuels as a way of reducing emissions from residential sources (Chinese State Council, 2013).

Semi-coke briquettes are industrial by-products made from bituminous raw-coal-chunks through a low-temperature carbonization process. These briquettes are being considered as a possible replacement of raw coals for residential usage (MEP, 2016), but knowledge on the emission from them is very limited (Li et al., 2016a, 2016b), and this complicates the evaluation process. Li et al. (2016a, 2016b) reported emission factors (EFs) of primary $PM_{2.5}$, particulate carbon, benzo [a] pyrene equivalent carcinogenic potency (BaP_{eq}), carbon monoxide (CO), carbon dioxide (CO_2) and sulfur dioxide (SO_2) emissions from household use of semi-coke briquettes. However, information on emissions of water-soluble ions, elements and nitrogen oxides ($NO_x = NO + NO_2$, a gas precursor of secondary $PM_{2.5}$) from semi-coke briquettes has not been obtained, and that information is needed to fully assess the feasibility of replacing raw coals with semi-coke briquettes.

In this study, we documented the EFs of primary $PM_{2.5}$ and selected chemical components, as well as trace gases including NO_x and SO_2 from residential coal combustion using custom-made combustion chamber. Seven coal samples were used in the tests, including one typical semi-coke briquette, its parent material and five traditional coals widely used in BTH. The major objective for the study was to estimate the emission reductions in BTH that might be achieved by replacing raw coals with semi-coke briquettes. To do this, the total emission reductions of primary $PM_{2.5}$ and trace gases were calculated, and the spatial distributions of the effects were modeled.

2. Experimental section

2.1. Fuel and stove

Selected properties by proximate and ultimate analysis of the seven coals tested in our study are presented in Table 1. The analyses of the materials were performed by Shaanxi Coal Geological Laboratory Co., Ltd., China using the national standards of the People's Republic of China (GB/T 211–2007, GB/T 212–2008 and GB/T213–2008). Semi-coke briquettes, which are the focus of this study, are made from the unprocessed

Table 1

Coal properties by proximate and ultimate analysis.

| Type | Semi-coke | | Bituminous | | Anthracite | | Anthracite | |
|---------------------------|-----------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|--|
| | briquette | | raw-coal-chunk | | raw-coal-chunk | | coal-briquette | |
| Coal ID | S-1 | Bc-1 ^a | Bc-2 ^b | Bc-3 ^b | Ac-1 ^b | Ab-1 ^b | Ab-2 ^b | |
| proximate analysis (wt%) | | | | | | | | |
| moisture* | 4.26 | 4.56 | 7.98 | 19.47 | 4.06 | 3.00 | 4.08 | |
| ash* | 14.06 | 10.82 | 7.98 | 10.56 | 11.06 | 32.34 | 35.98 | |
| volatile matter* | 4.32 | 31.26 | 33.2 | 24.56 | 7.22 | 4.99 | 5.04 | |
| fixed carbon* | 77.36 | 55.81 | 50.84 | 45.41 | 77.66 | 59.67 | 54.90 | |
| calorific value (MJ/kg)** | 24.01 | 24.87 | 25.82 | 20.02 | 28.56 | 20.37 | 18.48 | |
| ultimate analysis (wt%) | | | | | | | | |
| C* | 75.08 | 75.39 | 67.38 | 56.61 | 76.75 | 58.84 | 53.88 | |
| H* | 0.76 | 4.07 | 3.74 | 2.26 | 2.28 | 0.84 | 0.80 | |
| O* | 4.85 | 12.11 | 11.80 | 9.77 | 4.64 | 4.18 | 4.20 | |
| N* | 0.58 | 0.92 | 0.94 | 0.67 | 0.86 | 0.48 | 0.67 | |
| S* | 0.41 | 0.29 | 0.18 | 0.66 | 0.35 | 0.32 | 0.39 | |

* based on air-dry basis.

** as received.

^a The parent material used for producing semi-coke briquette (S-1).

^b Traditional coals used in the Beijing-Tianjin-Hebei (BTH) region.

bituminous raw-coal-chunks by a low temperature coal carbonization process (500–800 °C) in a pyrolyzing furnace. Various substances in the coal vaporize or turn into liquid-phase tar and solid-phase semi-coke at specific temperatures. We collected one semi-coke briquette (S-1) and its parent material (bituminous raw-coal-chunk, Bc-1) from Yulin city, where is the biggest producing bases of semi-coke briquettes in China. Five coal samples were also purchased at local markets in BTH to obtain regionally representative coals used in household; these were two bituminous raw-coal-chunks (Bc-2 and Bc-3), one anthracite raw-coal-chunk (Ac-1) and two anthracite coal-briquettes (Ab-1 and Ab-2).

The test stove in this study was of a type widely used in Northern China for residential cooking and heating, and it was bought from a local market. The stove was 50 cm high, and its hearth had an outer diameter of 24 cm and an inner diameter of 12 cm. There was a 6 cm diameter air-control lip near the bottom, which was fully open during the combustion experiments to allow the maximum amount of air to enter the stove (Fig. S1).

2.2. Sampling and analysis

The experiments were conducted in a combustion chamber system

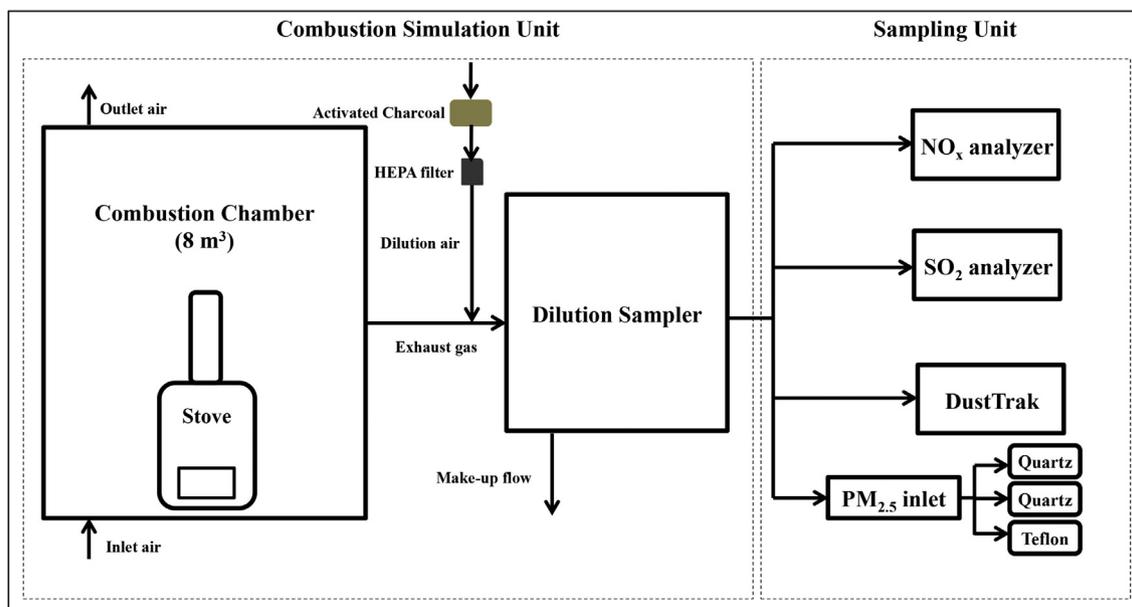


Fig. 2. Schematic of the combustion chamber system for residential coal combustion simulation.

(Tian et al., 2015), and the tests were designed to simulate the full residential coal combustion cycle from the ignition to the extinction of the fire (Fig. 2). The system consists of an 8 m³ chamber that was equipped with sensors for temperature, pressure and flow velocity, and a dilution sampler that was used for the aerosol and gas collections (Wang et al., 2012). The test stove was located in the combustion chamber, and the PM_{2.5} in the chamber was monitored in real time with a DustTrak (Model 8543, TSI Inc., Shoreview, MN, USA) (Wang et al., 2009). Before the actual sampling started, one honeycomb coal briquette was ignited in the stove and left to burn until its emitted primary PM_{2.5} was < 2 μg m⁻³ (0.2–5% of average PM_{2.5} concentrations during the whole burning cycle). Then pre-weighed tested coals (60–2000 g) were put into the stove and ignited by the honeycomb coal briquette to begin the test. The PM_{2.5} samples were collected on three parallel 47-mm filters at 5 L min⁻¹ flow rate, including one Teflon™-membrane filter (R2PJ047, Pall Life Sciences, Ann Arbor, MI, USA) for gravimetric and elemental analysis, and two quartz microfiber filters (QM/A, Whatman, Midstone, Kent, England) for organic carbon (OC), element carbon (EC), water-soluble ions and polycyclic aromatic hydrocarbon components (PAHs) analyses. Quartz filters were pre-cleaned at 900 °C for 3 h to remove adsorbed organic vapors (Watson et al., 2009). The NO_x and SO₂ concentrations in the diluted plume were continuously monitored at 1-s resolution by NO_x analyser (EC9841, Ecotech Pty Ltd, Australia) and SO₂ analyser (EC9850, Ecotech Pty Ltd, Australia), respectively. Details of the sampling were described in Tian et al. (2017). In this study, a total of 30 tests were conducted and at least three parallel tests were adopted for each type of coal samples. The dilution ratios were set at ~5–10 to provide the appropriate pollutant concentration level for on-line monitoring instruments and filter loadings. The sampling period typically lasted from 4 to 8 h, and this was adjusted based on the mass of the test coal sample.

For the gravimetric analyses, the filters were equilibrated at constant temperature (~25 °C) and relative humidity (~35%), and they were weighed before and after sampling by a high precision electronic balance with a ± 1 μg sensitivity (ME 5-F, Sartorius, Göttingen, Germany). The OC and EC were measured with a Desert Research Institute (DRI) Model 2001 Thermal/Optical Carbon Analyser (Atmoslytic Inc., Calabasas, CA, USA) following the IMPROVE_A thermal/optical protocol. Water-soluble NO₃⁻ and SO₄²⁻ were determined by an Ion Chromatograph (Dionex 600, Thermal Scientific-Dionex, Sunnyvale, CA, USA). Six elements (arsenic (As), cadmium

(Cd), chromium (Cr), lead (Pb), manganese (Mn) and nickel (Ni)) in the U.S. EPA hazardous air pollutants (HAPs) list were determined by energy-dispersive X-ray fluorescence (ED-XRF) spectrometry (PANalytical Epsilon 5, Almelo, The Netherlands) and combined as hazardous trace elements (HTEs) in the study (French et al., 1994; Tian et al., 2013). In-injection port thermal desorption coupled with gas chromatography/mass spectrometry (Agilent 7890/5975C-Gas Chromatography/Mass Spectrometer, Santa Clara, CA, USA) was used to quantify the concentrations of 16 U.S. Environmental Protection Agency (EPA) priority PM_{2.5}-bound PAHs (hereinafter as PAHs). The PAHs included naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorine (FLO), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), benz(a)anthracene (BaA), chrysene (CHR), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), dibenz (a,h)anthracene (DahA), indeno (1,2,3-cd)pyrene (IcdP) and benzo (g,h,i)perylene (BghiP). Details on these measurements were described in Chow et al. (2007), Chow and Watson (1999, 2017) and Wei et al. (2015).

2.3. Determination of EFs and modified combustion efficiency (MCE)

Emission factors (EFs) had been defined as the amount of a pollutant emitted per unit of fuel consumed (g kg⁻¹) (Delmas et al., 1996; Watson et al., 2012). For particulate pollutants (e.g., OC, EC, water-soluble ions, elements, etc.), the EF_p is calculated as:

$$EF_p = \frac{m_{particle} \times DR \times t_{sample} \times V_{Stk} \times D}{Q_{filter} \times m_{fuel}} \quad (1)$$

where $m_{particle}$ is the mass of the substance of interest on the filter (mg); DR is the dilution ratio, which is controlled by the flow balance of the dilution sampler, and can be calculated by dividing total inflow (equals total outflow) by sample flow of the dilution sampler (Tian et al., 2015); V_{Stk} is the stack flow velocities (m s⁻¹); D is the stack cross-sectional area (m²); Q_{filter} is the sampling volumes (m³) over the entire sampling duration (t_{sample} in s), and m_{fuel} is the mass of burned coal samples (g).

For NO_x and SO₂, the time-integrated EF_g is calculated as:

$$EF_g = \frac{\sum_{t=1}^{t=sample} C_{gas,t} \times DR \times V_{Stk} \times D}{m_{fuel}} \quad (2)$$

where $C_{gas,t}$ is the diluted concentration of trace gases at time t in mg m⁻³, and the other variables are as defined in equation (1).

Emissions vary with different combustion conditions, that is, whether the fire is flaming or smoldering, and these differences in conditions are reflected in the MCE. MCE is typically close to unity during the flaming phase, and it ranges between 0.7 and 0.9 for the smoldering phase (Reid et al., 2005; Yokelson et al., 1997). The MCE is calculated as follows:

$$\text{MCE} = \frac{\Delta\text{CO}_2}{\Delta\text{CO}_2 + \Delta\text{CO}} \quad (3)$$

where ΔCO_2 and ΔCO were the excess molar mixing ratios of CO_2 and CO , respectively. CO_2 and CO concentrations of the diluted smokes were monitored by CO_2 sensors (PP Systems, Amesbury, MA, USA) and a CO analyser (Thermo 48i, Thermo Scientific Inc., Franklin, MA, USA).

2.4. Emission reduction estimate and allocation

Total emission reductions of each pollutant i (E_i) that could be achieved by replacing raw coals with alternative coals in BTH for 2015 are estimated as follows:

$$E_i = (\text{EF}_{B,i} - \text{EF}_{R,i}) \times M_B + (\text{EF}_{A,i} - \text{EF}_{R,i}) \times M_A \quad (4)$$

where $\text{EF}_{B,i}$, $\text{EF}_{A,i}$ and $\text{EF}_{R,i}$ are the measured emission factors of pollutant i for bituminous raw-coal-chunk, anthracite raw-coal-chunk and alternative coals (semi-coke briquette or anthracite coal-briquette) in BTH, respectively; M_B and M_A are the amounts of the bituminous and anthracite raw-coal-chunk consumed in the residential sector in BTH during 2015. The values for these variables were obtained from China Energy Statistical Yearbook (2016), and they are summarized in Supplemental Table S1.

Based on the proxy variables (urban and rural population) collected from the fifth population census of National Bureau of Statistics (2000), the county-level pollutant emission reductions in BTH are calculated using the following equation:

$$E_{i,j} = \frac{P_j}{\sum_{j=1} P_j} \times E_j \quad (5)$$

where $E_{i,j}$ is the pollutant i emission reduction in county j of the BTH region; P_j is proxy variable in county j ; E_i is the emission reduction of pollutant i in BTH.

After allocating the regional emissions to 164 counties, the county-level pollutant emission reduction inventories were further disaggregated to grids at a resolution of $10 \text{ km} \times 10 \text{ km}$. The ratios of the area in each cell to total county area were calculated to allocate the emission of the county to each grid cell. If a grid cell contained more than one county, the emission of that grid cell is the sum of the emission from the different counties based on the calculated ratios.

3. Results and discussion

3.1. Primary $\text{PM}_{2.5}$ and trace gas emissions

3.1.1. Speciated primary $\text{PM}_{2.5}$ emission factors

In this study, the combustion experiments were dominated by flaming but mixed with some smoldering phase, with the time-averaged MCEs ranging from 0.89 to 0.95 (Table 2). Emission factors (EFs) of primary $\text{PM}_{2.5}$ mass and selected chemical components (OC, EC, PAHs, SO_4^{2-} , NO_3^- and HTEs) from burning of semi-coke briquette (S-1), its parent material (bituminous raw-coal-chunk, Bc-1) and five representative coals used in BTH (Bc-2, Bc-3, Ac-1, Ab-1 and Ab-2) are summarized in Table 2.

EFs for semi-coke briquette (S-1) and its parent material (bituminous raw-coal-chunk, Bc-1) The arithmetic mean (\pm standard deviation) EFs of burning semi-coke briquette S-1 were $0.75 \pm 0.19 \text{ g kg}^{-1}$ for primary $\text{PM}_{2.5}$, $0.15 \pm 0.01 \text{ g kg}^{-1}$ for OC, $0.02 \pm 0.01 \text{ g kg}^{-1}$ for EC and $0.96 \pm 0.48 \text{ mg kg}^{-1}$ for PAHs, respectively. These amounted to 4.18%,

2.27%, 0.28% and 0.04%, respectively, of matching EFs obtained from burning unprocessed Bc-1 ($17.93 \pm 2.24 \text{ g kg}^{-1}$ for primary $\text{PM}_{2.5}$, $6.60 \pm 2.01 \text{ g kg}^{-1}$ for OC, $7.17 \pm 0.76 \text{ g kg}^{-1}$ for EC and $2371 \pm 240 \text{ mg kg}^{-1}$ of PAHs). Previous studies had shown that volatile substances were important sources of primary particle matter (PM), OC, EC and PAHs, and their EFs had been found to increase with enlarged volatile content (Chen et al., 2015; Li et al., 2016c). The significant lower (student's t -test, $p < 0.05$, Table S2) EFs of primary $\text{PM}_{2.5}$, OC, EC and PAHs for S-1 relative to its parent material can be explained by lower volatile content of S-1 (4.32%, Table 1), compared with 31.26% for Bc-1. Indeed, as noted above, most of volatile matters in the parent material of bituminous raw-coal-chunk were removed through the carbonization process (See details in Section 2.1).

As shown in Table 2, the EFs of SO_4^{2-} and NO_3^- from S-1 combustion tests were $204 \pm 83 \text{ mg kg}^{-1}$ and $3.89 \pm 0.77 \text{ mg kg}^{-1}$, respectively, and these values were lower and significantly different (student's t -test, $p < 0.05$, Table S2) from those for Bc-1 ($529 \pm 78 \text{ mg kg}^{-1}$ for SO_4^{2-} and $112 \pm 3 \text{ mg kg}^{-1}$ for NO_3^-). Based on the set up of our sampling system (Section 2.2), we concluded that the measured SO_4^{2-} and NO_3^- in the emissions were dominated by primary particles. That is, it took only $\sim 15 \text{ s}$ for the smoke emitted from the stove to be collected on the filters, and there were no conditions, such as relative high humidity, UV lights, etc., that would favor the conversion of SO_2 or NO_x to their particulate forms. The EF of HTEs for S-1 was $5.50 \pm 0.60 \text{ mg kg}^{-1}$, and that was about one-fifth of that from burning Bc-1 ($25.02 \pm 2.62 \text{ mg kg}^{-1}$) with statistically significant difference (student's t -test, $p < 0.05$, Table S2). The differences in EFs of SO_4^{2-} , NO_3^- and HTEs might be partly explained at least in part by the different contents of sulfate, nitrogen and trace elements in different type of coals, but differences in combustion conditions also may have affected the results (Tian et al., 2013).

EFs for semi-coke briquette (S-1) and representative coals used in BTH For the assessment of emissions from semi-coke briquette (S-1), a series of tests were conducted for five coals used in residences in BTH. Relatively large variations had been found for particles emitted from burning of bituminous raw-coal-chunks, and that had been explained by differences in the coal's properties (Chen et al., 2005). As shown in Table 2, the average EFs of primary $\text{PM}_{2.5}$, OC, EC and PAHs for Bc-3 were $3.88 \pm 0.85 \text{ g kg}^{-1}$, $1.70 \pm 0.30 \text{ g kg}^{-1}$, $0.89 \pm 0.55 \text{ g kg}^{-1}$ and $198 \pm 69 \text{ mg kg}^{-1}$, respectively. In comparisons, Bc-2 presented higher EFs of primary $\text{PM}_{2.5}$, OC, EC and PAHs; these ranged from 4 to 12 times higher than those for Bc-3. The average EFs of primary $\text{PM}_{2.5}$, OC, EC and PAHs from burning of bituminous raw-coal-chunks (Bc-2 and Bc-3) were 14, 20, 286 and 1078 times higher than those of semi-coke briquette (S-1).

The average EFs for anthracite raw-coal-chunk (Ac-1) were $0.45 \pm 0.09 \text{ g kg}^{-1}$ for primary $\text{PM}_{2.5}$, $0.10 \pm 0.02 \text{ g kg}^{-1}$ for OC, $0.02 \pm 0.00 \text{ g kg}^{-1}$ for EC and $1.16 \pm 0.92 \text{ mg kg}^{-1}$ for PAHs, respectively. Anthracite coal-briquettes (Ab-1 and Ab-2) had slightly higher EFs than anthracite raw-coal-chunk (Ac-1), that is, $1.21 \pm 0.44 \text{ g kg}^{-1}$ for primary $\text{PM}_{2.5}$, $0.16 \pm 0.04 \text{ g kg}^{-1}$ for OC, $0.04 \pm 0.01 \text{ g kg}^{-1}$ for EC and $2.49 \pm 1.47 \text{ mg kg}^{-1}$ for PAHs, respectively. This may have been due to different coal shapes (chunk or briquette), and consistently higher MCE for Ac-1 compared with Ab-1 and Ab-2. Except OC EF for S-1 was statistically higher than that for Ac-1, the EFs of primary $\text{PM}_{2.5}$, OC, EC and PAHs showed no significant differences (student's t -test, $p > 0.05$, Table S2) between anthracite coal (Ac-1, Ab-1 and Ab-2) and semi-coke briquette (S-1).

The average SO_4^{2-} EF for S-1 was $204 \pm 83 \text{ mg kg}^{-1}$, and that was similar to the average value for the bituminous raw-coal-chunks ($204 \pm 74 \text{ mg kg}^{-1}$, Bc-2 and Bc-3), but a factor of two higher than the $123 \pm 54 \text{ mg kg}^{-1}$ for anthracite raw-coal-chunk (Ac-1) and lower than the $363 \pm 162 \text{ mg kg}^{-1}$ for anthracite coal-briquettes (Ab-1 and Ab-2). The EFs of NO_3^- and HTEs were $84.27 \pm 22.65 \text{ mg kg}^{-1}$ and $10.69 \pm 5.04 \text{ mg kg}^{-1}$ for bituminous raw-coal-chunks (Bc-2 and Bc-3), $17.35 \pm 4.77 \text{ mg kg}^{-1}$ and $8.65 \pm 4.31 \text{ mg kg}^{-1}$ for anthracite coal-briquettes (Ab-1 and Ab-2), $9.55 \pm 1.09 \text{ mg kg}^{-1}$ and $7.78 \pm 2.80 \text{ mg kg}^{-1}$ for anthracite raw-coal-chunk (Ac-1) and $3.89 \pm 0.77 \text{ mg kg}^{-1}$ and

Table 2

Modified combustion efficiency (MCE) and averaged emission factors of the major pollutants in primary PM_{2.5} from coal combustion in this study (based on dry-ash-free basis).

| Collection area | Coal ID ^a | MCE | Emission factors | | | | | | | |
|-----------------|--|-------------|--------------------------|--------------|--------------|---------------------------|-------------------------------|------------------------------|---------------|--------------|
| | | | PM _{2.5} | OC | EC | PAHs* | SO ₄ ²⁻ | NO ₃ ⁻ | HTEs** | |
| | | | Unit: g kg ⁻¹ | | | Unit: mg kg ⁻¹ | | | | |
| Yulin | S-1 | 0.92 ± 0.01 | 0.75 ± 0.19 | 0.15 ± 0.01 | 0.02 ± 0.01 | 0.96 ± 0.48 | 204 ± 83 | 3.89 ± 0.77 | 5.50 ± 0.60 | |
| | Bc-1 ^b | 0.91 ± 0.05 | 17.93 ± 2.24 | 6.60 ± 2.01 | 7.17 ± 0.76 | 2371 ± 240 | 529 ± 78 | 112 ± 3 | 25.02 ± 2.62 | |
| BTH | Bc-2 | 0.91 ± 0.03 | 18.35 ± 2.72 | 4.54 ± 0.71 | 10.56 ± 2.37 | 2292 ± 224 | 177 ± 25 | 91.93 ± 27.41 | 11.16 ± 6.59 | |
| | Bc-3 | 0.94 ± 0.02 | 3.88 ± 0.85 | 1.70 ± 0.30 | 0.89 ± 0.55 | 198 ± 69 | 231 ± 103 | 76.61 ± 18.85 | 10.21 ± 4.40 | |
| | Average of bituminous raw-coal-chunks ^c | | | 11.12 ± 8.13 | 3.12 ± 1.63 | 5.73 ± 5.51 | 1035 ± 1153 | 204 ± 74 | 84.27 ± 22.65 | 10.69 ± 5.04 |
| | Ac-1 | 0.95 ± 0.08 | 0.45 ± 0.09 | 0.10 ± 0.02 | 0.02 ± 0.00 | 1.16 ± 0.92 | 123 ± 54 | 9.55 ± 1.09 | 7.78 ± 2.80 | |
| | Ab-1 | 0.90 ± 0.05 | 0.92 ± 0.14 | 0.19 ± 0.06 | 0.04 ± 0.02 | 3.01 ± 2.31 | 224 ± 27 | 21.29 ± 1.82 | 8.55 ± 0.52 | |
| | Ab-2 | 0.89 ± 0.03 | 1.50 ± 0.48 | 0.14 ± 0.01 | 0.04 ± 0.01 | 1.80 ± 0.07 | 501 ± 32 | 13.42 ± 1.74 | 8.76 ± 7.44 | |
| | Average of anthracite coal-briquettes | | | 1.21 ± 0.44 | 0.16 ± 0.04 | 0.04 ± 0.01 | 2.49 ± 1.47 | 363 ± 162 | 17.35 ± 4.77 | 8.65 ± 4.31 |

* PAHs was the sum of 16 PM_{2.5}-bound PAH components, including NAP, ACY, ACE, FLO, PHE, ANT, FLA, PYR, BaA, CHR, BbF, BkF, BaP, DahA, IcdP and BghiP.

** Hazardous trace elements (HTEs) included six trace elements (As, Cd, Cr, Pb, Mn and Ni) in this study.

^a See Table 1 for Coal ID.

^b The parent material used for producing semi-coke briquette (S-1).

^c Average of Bc-2 and Bc-3.

5.50 ± 0.60 mg kg⁻¹ for semi-coke briquette (S-1) in descending order, respectively. The decrease of NO₃⁻ EFs for semi-coke briquette was significant at $p < 0.05$ (student's *t*-test, Table S2) compared to all the five coals used in BTH. Significant differences in the EFs for SO₄²⁻ and HTEs only existed between the semi-coke briquette and anthracite coal-briquettes (student's *t*-test, $p = 0.019$ for SO₄²⁻ from Ab-1 and $p = 0.011$ for HTEs from Ab-2, Table S2), which may be caused by additives in briquetting process (e.g., sawdust, yellow mud, NaNO₃, KNO₃, etc.).

3.1.2. Trace gases emission factors

Primary emission data for trace gases are illustrated in Fig. 3. The NO_x EF from burning S-1 was 0.84 ± 0.18 g kg⁻¹, and that was significantly lower (student's *t*-test, $p < 0.05$) than that from burning the parent material, Bc-1 (3.18 ± 0.88 g kg⁻¹). The EF of NO_x for S-1 was also lower than those for the five representative coals used in BTH: 3.19 ± 0.89 g kg⁻¹ for bituminous raw-coal-chunks (Bc-2 and Bc-3), 1.67 ± 0.30 g kg⁻¹ for anthracite raw-coal-chunk (Ac-1) and 1.22 ± 0.25 g kg⁻¹ for anthracite coal-briquettes (Ab-1 and Ab-2). The NO_x EFs showed a weak but significant positive correlation with nitrogen (N) content in measured coals ($r^2 = 0.61$, $p < 0.05$). That is, the higher N contents in coals (Bc-1, Bc-2, Bc-3, Ac-1, Ab-1 and Ab-2) compared with S-1 evidently promoted the formation of NO_x in the burning process. Additionally, the semi-coke briquette has the relative lower volatile matter and ratio of oxygen to nitrogen (O/N) compared with bituminous coals (Table 1), which could impede the oxidation of N in the fuel to NO_x and cause less emission of NO_x (Hu et al., 2003).

The parent raw material for S-1 (Bc-1) can be considered a low-sulfur coal (< 1%, Table 1), and the primary objective of the development of the semi-coke briquette from this parent material was to reduce particulate emission. In fact, the SO₂ EF for S-1 was 2.41 ± 0.29 g kg⁻¹, and that is similar to the 2.80 ± 0.34 g kg⁻¹ for Bc-1. Further comparisons showed that the SO₂ EF for S-1 was comparable with those for Bc-2 (2.43 ± 0.41 g kg⁻¹), Bc-3 (3.06 ± 0.23 g kg⁻¹) and Ab-2 (2.35 ± 0.31 g kg⁻¹), but considerably lower than the average SO₂ EFs of 4.26 ± 1.12 g kg⁻¹ for Ac-1 and 5.31 ± 0.83 g kg⁻¹ for Ab-1. One might expect that the SO₂ emissions would have been directly proportional to the sulfur (S) contents of the fuels (Lu et al., 2010), but no significant correlation was

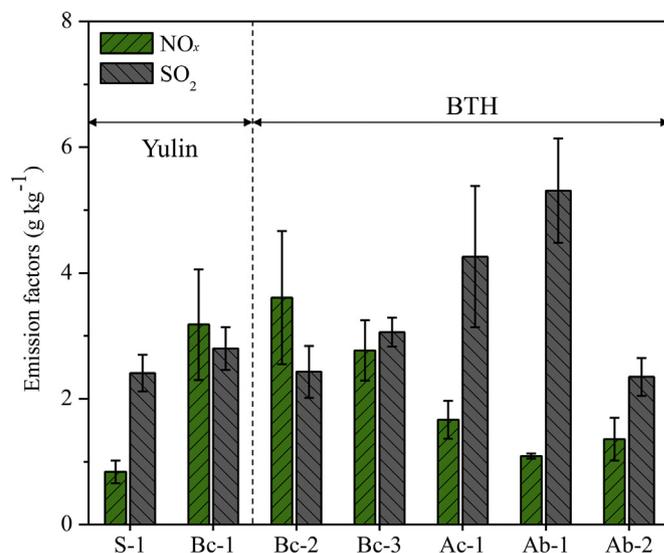


Fig. 3. Emission factors of NO_x and SO₂ from coal combustion. Semi-coke briquette (S-1) and its parent material (Bc-1) were collected from Yulin city. 2 bituminous raw-coal-chunks (Bc-2 and Bc-3), 1 anthracite raw-coal-chunk (Ac-1) and 2 anthracite coal-briquettes (Ab-1 and Ab-2) were obtained from the Beijing-Tianjin-Hebei (BTH) region.

found between these variables, indicating that the S content of the fuel may not be the only factor to determine the SO₂ emissions from low-sulfur coals burned in residences. Other factors, such as specific surface areas and sulfur retaining compounds (e.g., Ca(OH)₂ and CaO) in the coals, also could cause sulfur to be partitioned into the ash and lead to lower SO₂ emissions (Lee et al., 2005).

3.2. Comparisons with EFs from other studies

There are few measurements of emissions from burning semi-coke briquettes with which we can compare our results. Li et al. (2016a) reported EFs for semi-coke briquettes were 0.49 ± 0.18 g kg⁻¹ for primary

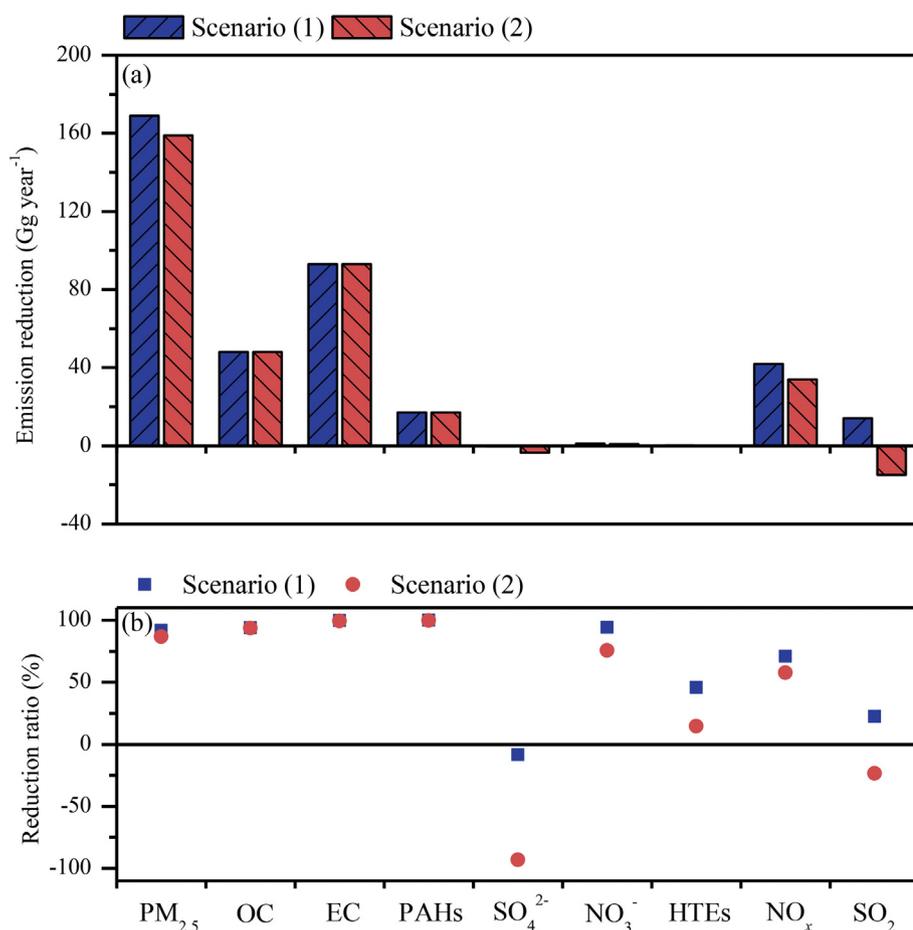


Fig. 4. Emission reduction estimates by replacing Beijing-Tianjin-Hebei (BTH)'s currently used raw coals (bituminous raw-coal-chunk and anthracite raw-coal-chunk) with semi-coke briquette (scenario (1)) or with anthracite coal-briquette (scenario (2)): (a) emission reduction (Gg year⁻¹); (b) reduction ratio (%), calculated by dividing the emission reduction by the emission from the currently used raw coals (bituminous raw-coal-chunk and anthracite raw-coal-chunk), with no clean coals applied.

PM_{2.5}, $0.194 \pm 0.127 \text{ g kg}^{-1}$ for OC and $0.012 \pm 0.008 \text{ g kg}^{-1}$ for EC, respectively. The EFs reported in that study were slightly lower than in ours, possibly due to the different types of stoves used in the studies. In fact, a traditional coal stove was applied in our study, whereas an advanced coal stove was used by Li et al. (2016a). Our study focused on comparisons of emission from various coal types rather than differences among the stoves, but the types of stoves and combustion conditions certainly could affect the quantities and types of emissions. The SO₂ EF measured in our study were $2.41 \pm 0.29 \text{ g kg}^{-1}$ for S-1, and that is comparable with $2.30 \pm 0.16 \text{ g kg}^{-1}$ for semi-coke briquettes burned in a traditional stove by Li et al. (2016b).

We also compiled available data in literature on EFs from residential coals burned in traditional stoves for comparisons with our results, and these data were summarized in Table S3 (Chen et al., 2006, 2015; Liu et al., 2009; Geng et al., 2014; Shen et al., 2010a, 2010b; Zhi et al., 2009). For bituminous coals, the average EFs for BTH's coals in the present study fall within the ranges of EFs for bituminous raw-coal-chunks (2.22 g kg^{-1} – 10.28 g kg^{-1} for primary PM_{2.5}, 0.104 g kg^{-1} – 17.01 g kg^{-1} for OC, 0.006 g kg^{-1} – 12.67 g kg^{-1} for EC and 2.62 mg kg^{-1} – $1077.2 \text{ mg kg}^{-1}$ for PAHs). For anthracite coals, our EF values also are of the same order as the data in the literature: 1.76 g kg^{-1} to 1.84 g kg^{-1} for primary PM_{2.5}, 0.007 g kg^{-1} to 0.08 g kg^{-1} for OC, 0.002 g kg^{-1} to 0.06 g kg^{-1} for EC and 1.4 mg kg^{-1} to 19.9 mg kg^{-1} for PAHs.

There have been a few studies of SO₂ EFs from residential coal combustion in China. Ge et al. (2004) reported SO₂ EFs of $4.51 \pm 2.05 \text{ g kg}^{-1}$ for honeycomb coal and $9.92 \pm 2.83 \text{ g kg}^{-1}$ for coal cake burned in the household stove. The difference in SO₂ EFs from our study (from 2.43 g kg^{-1} for Bc-2 to 5.31 g kg^{-1} for Ab-1 collected from the BTH region) and Ge et al. (2004) were likely due to higher sulfur contents for honeycomb coal and coal cake (1.31% and 1.58%, respectively) used in the work of Ge et al. (2004). Different coal shapes

also may have played a role. Furthermore, the SO₂ EFs from our study were different from those (8 g kg^{-1} to 69 g kg^{-1}) reported by Zhao et al. (2010) who sampled emissions from coal-fired power plants in China. This comparison suggests that less sulfur is retained in industrial combustion process compared with residential usages (Zhao et al., 2010). Information on the EFs of water-soluble ions, elements and NO_x from residential coal combustion in China is even more scarce than that for SO₂, and more studies on those substances are expected in the future.

3.3. Assessment of pollution reduction

To evaluate the reductions in primary PM_{2.5} and trace gases emissions that could result from coal replacement in BTH, we modeled two scenarios for benefit analysis: replacing the currently used raw coals (bituminous raw-coal-chunk and anthracite raw-coal-chunk) with either semi-coke briquette, a new type of clean coal (scenario (1)) or anthracite coal-briquette (scenario (2)) that recommended as a clean coal in China during last two decades (Zhi et al., 2009). The total emission reductions from residential coal combustion before and after switching to clean coals were calculated by multiplying EFs of each type of coal by corresponding coal consumptions amounts (equation (4)). Here we took average EFs of bituminous raw-coal-chunks (i.e., average of Bc-2 and Bc-3) and average EF of anthracite coal chunk (Ac-1) as EFs of traditional raw coals.

As shown in Fig. 4a, the total emission reductions under scenario (1) were 169 Gigagram (Gg) year⁻¹ for primary PM_{2.5}, 48 Gg year⁻¹ for OC, 93 Gg year⁻¹ for EC, 17 Gg year⁻¹ for PAHs, 1.33 Gg year⁻¹ for NO₃⁻, 0.09 Gg year⁻¹ for HTEs, 42 Gg year⁻¹ for NO_x and 14 Gg year⁻¹ for SO₂, respectively, and the total emission reductions under scenario (2) were 159 Gg year⁻¹ for primary PM_{2.5}, 48 Gg year⁻¹ for OC, 93 Gg year⁻¹ for

EC, 17 Gg year⁻¹ for PAHs, 1.07 Gg year⁻¹ for NO₃⁻, 0.03 Gg year⁻¹ for HTEs and 34 Gg year⁻¹ for NO_x, respectively. The calculations showed that replacements of the raw coals with semi-coke briquette and anthracite coal-briquette would lead to similar reductions in OC, EC, PAHs, but semi-coke briquette would produce greater reductions in primary PM_{2.5}, NO₃⁻, HTEs, NO_x and SO₂.

From the energy point of view, the energy consumed is based on the calorific value (Table 1) multiplying by fuel mass consumption and energy efficiency. Energy efficiency in household coal combustion indicated actual energy output ratio, and was assumed as 1 in this study. In the real world, it is mainly governed by heat transfer and combustion efficiencies and has a wide variety (Li et al., 2016b). The different matches of fuels and combustion method (i.e., stoves) should be investigated to improve our knowledge of energy efficiency and evaluate the reduction of pollutants in the future. In BTH for 2015, bituminous and anthracite raw-coal-chunks provided the energy of 4.92×10¹² MJ. Under scenario (1), semi-coke briquette substitution could produce almost the same amount of energy (4.91×10¹² MJ), while the energy production (3.97×10¹² MJ) decreased by replacing anthracite coal-briquettes under scenario (2). The results suggest that semi-coke briquette is more energy efficient than anthracite coal-briquette.

Monte Carlo simulation was used to assess uncertainties in the emission reduction estimates. Uncertainties in primary PM_{2.5} and trace gas emission reduction calculations mainly stemmed from two sources: the amount of coal usage and the EFs (Streets et al., 2003). With respect to the activity data, expert elicitation was used, and the probability of the value used for coal consumption was assumed to have a normal distribution with a coefficient of variation (CV) of 20% (Zhao et al., 2011). Based on our experiments, all the EFs were modeled as log-normal distribution with CVs expressed the standard deviation divided by the mean (Bond et al., 2004). With 10,000 times repeats of Monte Carlo randomly simulation, the propagation of uncertainty at the 95% confidence interval was obtained in Table 3, providing an uncertainty range of [-94%, 312%] for primary PM_{2.5}, [-77%, 180%] for OC, [-99%, 520%] for EC, [-98%, 468%] for PAHs, [-73%, 151%] for NO₃⁻, [-119%, 231%] for HTEs, [-60%, 91%] for NO_x and [-202%, 296%] for SO₂ under scenario (1), and an larger uncertainty range of [-100%, 330%] for primary PM_{2.5}, [-79%, 184%] for OC, [-99%, 526%] for EC, [-98%, 488%] for PAHs, [-90%, 190%] for NO₃⁻, [-1562%, 1242%] for HTEs and [-75%, 112%] for NO_x under scenario (2). Lower limits for the uncertainty range were less than -100%, suggesting that the pollutant emissions could probably increase.

Fig. 5 showed the spatial distributions (10 km × 10 km resolution) of the modeled reductions of pollutant emissions for BTH in 2015 that could have occurred if the raw coals were replaced with semi-coke briquette. High pollutant emission reductions were centered over the plains of Hebei province to the south of the Yan and Taihang Mountains, and low reductions were centered over the northern mountain

Table 3

Uncertainty ranges for emission reductions of primary pollutants in the Beijing-Tianjin-Hebei (BTH) region for 2015.

| Substance | Scenario (1) ^a | Scenario (2) |
|------------------------------|---------------------------|-----------------|
| PM _{2.5} | [-94%, 312%] | [-100%, 330%] |
| OC | [-77%, 180%] | [-79%, 184%] |
| EC | [-99%, 520%] | [-99%, 526%] |
| PAHs | [-98%, 468%] | [-98%, 488%] |
| NO ₃ ⁻ | [-73%, 151%] | [-90%, 190%] |
| HTEs* | [-119%, 231%] | [-1562%, 1242%] |
| NO _x | [-60%, 91%] | [-75%, 112%] |
| SO ₂ ** | [-202%, 296%] | |

* Hazardous trace elements (HTEs) included six trace elements (As, Cd, Cr, Pb, Mn and Ni) in this study.

** SO₂ emission increased under scenario (2).

^a See text for description of scenarios (1) and (2).

and plateau regions of Beijing and Hebei. The reductions of pollutant emissions estimated in this study had spatial distributions similar to the PM_{2.5} concentrations linked to residential coal combustion in BTH for 2015 as reported by Zhang et al. (2017), identifying the pollutant emission-reducing hot-spots in BTH for government. The agreement between the study of Zhang et al. (2017) and ours simply reflected the fact that the greatest reductions in pollution emissions would be achieved in those areas with the highest burdens of pollutants.

4. Summary and policy implications

Laboratory experiments using a combustion chamber were conducted to study emissions of primary PM_{2.5}, associated particulate species and trace gases (NO_x and SO₂) from residential burning of several types of coals. The coals used in the tests were one typical semi-coke briquette, its parent material and three types of traditional coals (bituminous raw-coal-chunk, anthracite raw-coal-chunk and anthracite coal-briquette) extensively used in BTH. Compared with the parent material (bituminous raw-coal-chunk), significant lower particulate EFs for semi-coke briquette were found in primary PM_{2.5}, OC, EC, PAHs, SO₄²⁻, NO₃⁻ and HTEs. This was mainly attributed to the lower volatile matter content in the semi-coke briquette, and that was due to the carbonization process used to produce them. NO_x EF for semi-coke briquette was also significant lower than that for the parent material, while SO₂ EFs were similar between them.

The main implication drawn from our study of residential coal combustion is that replacing traditional energy sources would improve regional air quality in BTH and these findings are likely applicable to other regions in China. The EFs for five commonly coals used in BTH were measured and compared with the semi-coke briquette, and the findings demonstrate that semi-coke briquette could be considered as an effective “clean coal” to bituminous coal. That is, reductions in primary PM_{2.5} (91.6%), OC (94.0%), EC (99.6%), PAHs (99.9%), NO₃⁻ (94.2%), HTEs (45.6%), NO_x (70.9%) and SO₂ (22.3%) can be realized if raw coals were replaced with semi-coke briquette (Fig. 4b). During 2015 the semi-coke production was ~25 Mt in Yulin. At current production capacity, semi-coke briquette can gradually replace raw coals in the most heavily polluted parts of the BTH region, such as the southern part region (Fig. 5). It is important to note that semi-coke briquette is roughly the same cost as bituminous raw-coal-chunks (420 CNY ton⁻¹ versus 395–480 CNY ton⁻¹), and it is cheaper than anthracite raw-coal-chunk (1100 CNY ton⁻¹) and anthracite coal-briquettes (450–550 CNY ton⁻¹) (Table S4). Therefore, there appears to be no economic barriers, and perhaps even benefits, to the large scale replacement of traditional coals with semi-coke briquette. It is worth noting, however, that the price of semi-coke briquettes fluctuates because the government has a strong influence on prices. Without financial subsidies, the economic advantages of semi-coke briquettes might be reduced or disappear. More detailed analyses of the costs and benefits of the large-scale conversion to semi-coke briquettes obviously are needed.

An ideal clean energy fuel would produce low pollutant emissions, be cost efficient and have a reliable supply chain. Our study showed some potential environmental and health benefits if raw coals were replaced with semi-coke briquettes in BTH. Nonetheless, we should notice that SO₄²⁻ emissions under the scenario (1) and (2) were higher for both semi-coke briquette and anthracite coal-briquette than raw coals. Aerosol sulfate plays an important role in the formation of haze and need to pay more attentions (Wang et al., 2016). Further work about primary SO₄²⁻ effective emission reductions on the atmospheric PM_{2.5} loading should be carried out, aiming at improving the quality of semi-coke briquette. Although semi-coke briquette might not be the perfect option of clean energy due to potentially high emissions of SO₄²⁻ and the risk of price instability, it may be an acceptable short- or long-term alternative to traditional raw coals. Switching from traditional raw coals to semi-coke briquettes may help reduce the emissions

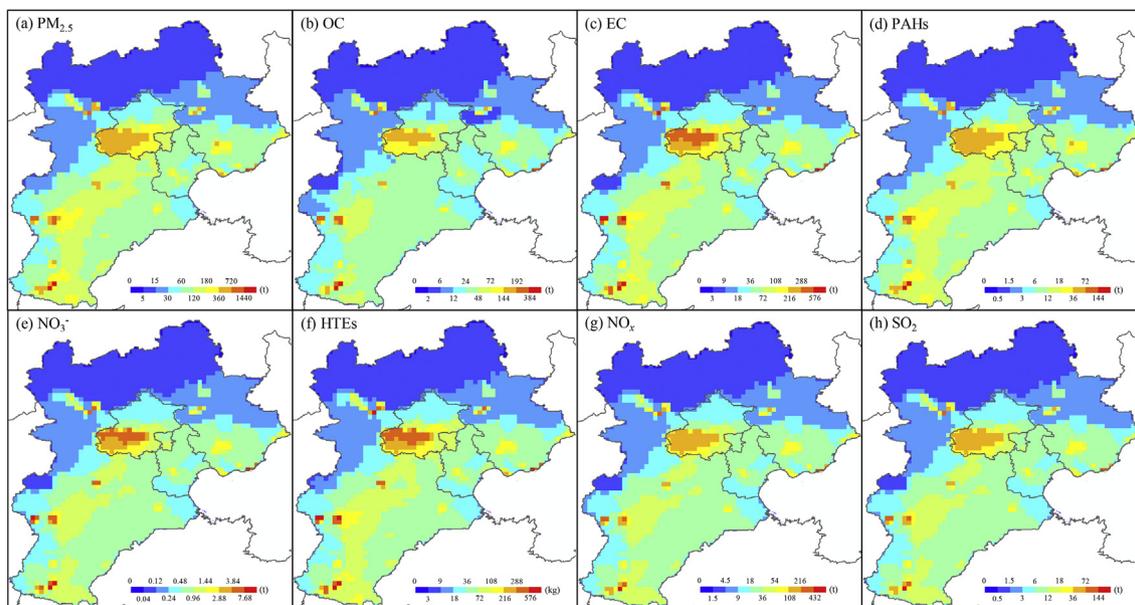


Fig. 5. Simulated spatial distribution (10 km \times 10 km) of primary $PM_{2.5}$ and trace gas emission reductions from replacing raw coals with semi-coke briquette in the Beijing-Tianjin-Hebei (BTH) region for 2015: (a) $PM_{2.5}$ (t); (b) OC (t); (c) EC (t); (d) PAHs (t); (e) NO_3^- (t); (f) HTEs (kg); (g) NO_x (t); (h) SO_2 (t).

of pollutants of concern in BTH and other regions in China, but further studies are needed to weigh the costs against the benefits more comprehensively.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.atmosenv.2018.07.031>.

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