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Emissions of fine particulate nitrated phenols from residential coal combustion in China

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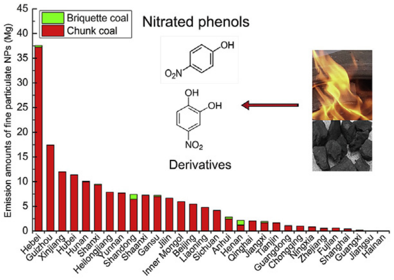
GRAPHICAL ABSTRACT



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ABSTRACT

Nitrated phenols (NPs) are regarded as a major component of brown carbon and affect the earth environment. Previous studies have suggested that NPs in the atmosphere partially originate from coal combustion; however, the direct emissions have not been validated. In this study, the emissions of ten NPs from ten kinds of coal for residential use were investigated via laboratory combustion experiments in which $PM_{2.5}$ samples were collected and analyzed by UHPLC-MS. The fine particulate NPs emitted from coal combustion were dominated by nitrocatechols and the methyl substituents under most conditions, while the emission profile of nitrated phenols varies with different rank of coals. Based on the emission ratios of NPs/$PM_{2.5}$ obtained from this study and the $PM_{2.5}$ emission factors in the literature, the emission factors of fine particulate NPs for chunks of lignite, bituminite, and anthracite and for briquettes of anthracite were calculated as 0.2–10.1 mg kg^{-1}. According to the residential coal consumption in 30 provinces in China in 2016, the total emission of fine particulate NPs from the residential coal combustion was estimated to be 178 ± 42 Mg.

1. Introduction

Nitrated phenols (NPs), organic molecules that consist of at least one nitro functional group and one hydroxyl group connected to an aromatic ring, are considered to be among the main components of brown carbon (BrC) (Desyaterik et al., 2013; Teich et al., 2017; Zhang et al., 2011). Recently, several studies indicated that nitrogen-containing organics are likely an effective BrC chromophores (Chen et al.,

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2018; Wang et al., 2017a,b; Xie et al., 2017). A field study showed that five NPs in the air mass which was influenced by biomass burning accounted for 4 ± 2% of particulate BrC light absorption at 370 nm measured in Detling, UK, 2012 (Mohr et al., 2013). The contribution of eight NPs to water-soluble BrC light absorption was estimated to be 4% in the Los Angeles Basin during 2010 field campaign (Zhang et al., 2013). The average contribution of NPs to water-soluble BrC light absorption ranged from 0.1 to 1.25% under acidic conditions and 0.1–3.7% under alkaline conditions over six campaigns in Germany and China from 2013 to 2014, which was five times higher than their mass contribution to aqueous extract BrC, implying the disproportionately high impact of NPs on the BrC light absorption properties (Teich et al., 2017).

Atmospheric NPs are generated not only from primary emissions, including biomass burning (Chow et al., 2015; Hoffmann et al., 2007; Iinuma et al., 2010), coal combustion (Lüttke et al., 1997), vehicle exhausts (Tremp et al., 1993) and the production and usage of pesticides and herbicides (Shafer and Schönherr, 1985), but also from the oxidation of phenols and benzenes in the gas phase and condensed phase in the presence of oxidants and nitrogen oxides (Grosjean, 1985; Harrison et al., 2005; Yuan et al., 2016). Due to their strong absorption of ultraviolet and visible light, NPs affect the atmospheric radiation balance and photochemistry and thus regional climates and air quality (Chakrabarty et al., 2016; Chen et al., 2018; Desyaterik et al., 2013; Mohr et al., 2013; Teich et al., 2017; Wang et al., 2017a,b; Xie et al., 2017). In addition, NPs can be absorbed through the cuticles of leaves or taken up by plant roots, and therefore hinder plant development by affecting the uptake of nutrients (Harrison et al., 2005; Shafer and Schönherr, 1985; Votrubová-Vaňousová, 1977). Moreover, the nitrated phenols was confirmed to have genotoxic effect on human body and Salmonella microorganism (Fernandez et al., 1992; Huang et al., 1995). Owing to these significant impacts of NPs on the climate, air quality, ecosystems, and human health, close attention has been paid to their sources and emission characteristics.

Previous field measurements have provided evidence that coal combustion is an important source of NPs and brown carbons in the atmosphere. The contents of NPs in air and cloud water were measured at the summit of Great Dun Fell, UK, in the spring of 1993, and the results showed that relatively high levels of NPs were related to high concentrations of both NO_x and SO_2, i.e., they were influenced by fresh coal combustion plumes (Lüttke et al., 1997). The chemical analysis of the organic fraction of $PM_{2.5}$ collected in urban Cork, Ireland, in September 2011 presented a large proportion of nitroaromatic compounds, which was attributed to intensive anthropogenic activities including domestic solid fuel burning (peat, coal, and wood) and vehicle emissions (Kourtchev et al., 2014). Recently, our field measurements at four sampling sites in northern China have indicated that the direct emissions from coal combustion and the aged coal combustion plume both contributed to a large fraction of the measured fine NPs in the atmosphere (Wang et al., 2018). Additionally, a laboratory study (Knobloch et al., 1999) identified gas-phase 2-nitrophenol in the combustion flue gas of brown-coal briquettes and obtained an emission factor of 1.5 mg kg^{-1}. Moreover, a preliminary estimation showed that the emission of BrC from residential coal burning was 95.2 ± 73.7 Gg in China, 2010 (Cai et al., 2014). The measured emission factors of BrC from seven coals combustion ranged from 1.08 ± 0.80 g kg^{-1} to 8.59 ± 2.70 g kg^{-1}, based on which the emission amount of BrC from residential coal combustion was estimated to be 592 Gg in China in 2013 (Sun et al., 2017). However, while it is clear that coal combustion contributes to the atmospheric NPs, no comprehensive understanding exists of the direct emissions of NPs from the combustion of various kinds of coal.

As one of the most important energy resources, coal is widely used around the world for power generation, industrial production, household cooking, heating, and so on (Schweinfurth, 2009). In China, total coal consumption reached 2702 Tg (1 Tg = 10^{12} g) in 2016, 91 Tg of which was used in the residential sector for cooking and heating from China Energy Statistics Yearbook 2017 (Department of Energy Statistics, China's National Bureau of Statistics, 2017). In the residential sector, due to the lack of particle removing apparatus and the low combustion efficiency, coal combustion releases large amounts of carbonaceous particles, such as organic carbon (OC), black carbon (BC), and BrC (Sun et al., 2017; Zhang and Smith, 2007), and it is therefore highly possible an important emission source of nitrated phenols. In the present study, ten species of NPs were detected in $PM_{2.5}$ samples collected from the combustion of ten kinds of coal. The emission profiles of fine particulate NPs from fresh coal combustion were presented. The emission ratios of NPs to $PM_{2.5}$ were calculated and were further used to estimate the emission factors and the emission amounts of fine NPs from the residential coal combustion in China in 2016.

2. Materials and methods

2.1. Coal selection

Ten kinds of coal with a wide range of geological maturity from three provinces of China (Inner Mongolia, Shanxi, and Shaanxi) were selected for the combustion experiments. They were all widely used in the residential sector (Chen et al., 2006), and included two lignite (raw lignite (LC1) and cleaned lignite (LC2)), four bituminite (non-coking coal (NBC), bottle coal (BBC), lean coal (LBC), and meager coal (MBC), in which the former two are high volatile bituminous coals and the latter two are low volatile bituminous coals), one natural coke (NCC), and three anthracites following the ASTM standard classification (ASTM, 2012). Detailed information on these kinds of coal is shown in Table 1. The rank of the selected coal, from low to high, was lignite, bituminite, and anthracite (Schweinfurth, 2009). There are three different anthracites and they were prepared in chunk (AC) and honeycomb briquette (AH1 and AH2), respectively, and other kinds of coal were all in chunks. The briquettes for residential use in China were

Table 1
Characteristics of ten kinds of coal used in this study.

Source region	Coal Name	Coal ID	Rank	Style	V_{daf},[a] %	R_0,[b] %
Inner Mongolia	Raw lignite	LC1	Lignite	Chunk	≥40	0.35
Inner Mongolia	Cleaned lignite	LC2	Lignite	Chunk	≥40	0.38
Shaanxi	Non-coking coal	NBC	Bituminite	Chunk	34	0.58
Shaanxi	Bottle coal	BBC	Bituminite	Chunk	35	0.55
Shanxi	Lean coal	LBC	Bituminite	Chunk	13	1.70
Shanxi	Meager coal	MBC	Bituminite	Chunk	14	1.98
Shanxi	Natural coke	NCC	–	Chunk	–	7.38
Shanxi	Anthracite	AC	Anthracite	Chunk	8	2.03
Shanxi	Anthracite	AH1	Anthracite	Briquette	–	–
Shanxi	Anthracite	AH2	Anthracite	Briquette	–	–

[a] Volatile matter on dry and ash-free basis.

[b] The virtrinite reflectance of coal.

usually made from anthracite coal due to the low fraction of volatile compounds and the little smoke when burnt, and thus two anthracite briquettes were selected. The coal chunks were 3–6 cm in equivalent diameter and the briquettes were shaped in 12-hole columns with a height of 7.5 cm and diameter of 10 cm.

2.2. Sampling system

The sampling system shown in Fig. S1 consisted of combustion stove, particle-flow cooling/dilution tunnel, exhaust duct, sampling chamber, $PM_{2.5}$ sampler, and air blower. Two stoves were deployed in the combustion experiments, including a traditional stove used for the eight kinds of chunk coal and a common briquette coal stove used for the two anthracite honeycomb briquettes. The steel particle-flow cooling/dilution tunnel was used to cool down the flue gas and transport it to the sampling chamber. The exhaust duct was used to release the rest of flue gas to the outdoor atmosphere. The sampling chamber was made of glass with a volume of approximately 50 L. A medium-volume $PM_{2.5}$ sampler (TH-150, Wuhan Tianhong, China), the size-selective inlet of which was installed in the sampling chamber, was used to collect fine particulate matter in the flue gas onto 88-mm quartz-fiber filters at a flow rate of $100\,L\,min^{-1}$. An air blower was installed at the downstream end of the cooling/dilution tunnel to provide particle-free air to clean the sampling system or to dilute the flue gas. More detailed description can be seen in our previous study (Wang et al., 2017a,b).

2.3. Sampling procedure

During the combustion experiments, a small amount of chunk or briquette coal was ignited outdoors using grass and branches. Then, the burning coal was transferred into the stove and 3 kg of fresh coal was added. To check whether there was any difference between different burning conditions, the combustion of coal was divided into early and later stages (Bond et al., 2002) and 2 $PM_{2.5}$ samples were collected successively in each stage without further dilution. These two stages were divided mainly based on the fraction of new coal and the intensity of the flame. During the first 15–30 min in the early stage, there was a lot of new coal, i.e., more than half of the coal in the stove was in black on the surface, and the burning flame was vigorous due to the high levels of volatile components. The stove temperature was in the range of 750–950 °C and the collected fine particulate matter was tawny-colored. After 15–30 min, the amount of new coal significantly decreased, and the flame intensity and the smoke density gradually weakened. In the later stage, the stove temperature was a little lower, ranging from 650 to 900 °C. The collected particulate matter had the color of apricot cream. Overall, the early stage in this study corresponded to the period/condition when new coal was added into the burning stove for residential use and the subsequent period/condition when a large fraction of new coal remained in the stove, while the later stage corresponded to the period/condition when there was a few or no new coal in the stove. Before collection, for each coal and at each stage, the tunnels and the sampling chamber were cleaned for 10 min with particle-free air. The collection of each sample lasted for 20–300s (mostly 30–120s for the early stage and 60–300s for the later stage) depending on the combustion situation and the smoke density. The mass concentrations of the $PM_{2.5}$ were determined by weighing the sample filters before and after sampling with an electronic microbalance (ME5, Sartorius, Germany) in a weighing room. The combustion experiment was repeated twice to capture the emission variability. As a consequence, there were totally 8 $PM_{2.5}$ filter samples for each coal in two stages. To examine the potential influence to $PM_{2.5}$ samples from laboratory air, flue air in the chamber, and gas-phase NPs in the flue gas due to absorption, blank filter samples were prepared separately in the laboratory and in the chamber without sampling and in the chamber immediately after the normal sample filter with the sampler working.

2.4. Sample pretreatment and analysis methods

The collected $PM_{2.5}$ filter samples were cut into two halves. The NPs and other organic matter in one half of each filter sample were extracted with methanol using an ultrasonic bath. After sonication, the extract solution was concentrated using a non-heated rotary evaporator and the filtrated concentrate was then blown to near dryness with a moderate flow of high-purity nitrogen. Finally, the residue was re-dissolved in 300 μL methanol containing $200\,\mu g\,L^{-1}$ 2,4,6-trinitrophenol as internal standard. In addition, an area of $2\,cm^2$ of the $PM_{2.5}$ filter sample was cut out, and the contents of OC and elemental carbon (EC) were measured by the thermal-optical method (Sunset, OCEC analyzer, USA), which abided by the NIOSH 5040 protocol and used the thermal-optical transmittance (TOT) method. The OM concentration was estimated by multiplying the OC content by a factor of 1.3 (Chen et al., 2006).

The NPs in the sample solution were detected by ultrahigh performance liquid chromatography (UHPLC, UltiMate 3000, Thermo Scientific, USA) coupled to a trap mass spectrometer (MS, LCQ Fleet, Thermo Scientific, USA) equipped with an electrospray ionization (ESI) source. The chromatographic analysis of the target NPs was conducted on an Atlantics T3 C18 column (2.1 mm × 150 mm, 3 μm, 100 Å). The mobile phase consisted of methanol containing 11% acetonitrile and water containing 11% acetonitrile and 0.1% formic acid, was supplied at a flow rate of $0.2\,mL\,min^{-1}$. More information on the sample pretreatment and analysis can be found in our previous study (Wang et al., 2017a,b). Negative polarity in the selected ion monitoring (SIM) mode was used to detect the following ten NPs: 4-nitrophenol (4NP), 3-methyl-4-nitrophenol (3M4NP), 2-methyl-4-nitrophenol (2M4NP), 4-nitrocatechol (4NC), 4-methyl-5-nitrocatechol (4M5NC), 3-methyl-6-nitrocatechol (3M6NC), 3-methyl-5-nitrocatechol (3M5NC), 5-nitrosalicylic acid (5NSA), 3-nitrosalicylic acid (3NSA), and 2,4-dinitrophenol (2,4DNP). Note that these ten NPs were selected as they were the most common and most abundant nitrated phenolic compounds in smoke plumes and in atmosphere (Iinuma et al., 2010; Claeys et al., 2012; Kitanovski et al., 2012a, 2012b; Mohr et al., 2013; Satoshi Inomata et al., 2015). Other common NPs or isomers of 2-nitrophenol and nitroguaiacols were not detected in this study, because they were undetectable or below the detection limit in our samples – such situation could also be seen in some recent field determinations (Chow et al., 2015; Kitanovski et al., 2012b; Teich et al., 2014). The quantification of the target NPs was conducted using internal standards and multi-point standard curves of analytes. Most of the chemicals were ordered from Sigma-Aldrich (St. Louis, MO, USA) and some were from J&K Chemical (Beijing, China) and Atomax Chemicals (Shenzhen, China). The recovery rates of the ten nitrated phenols were determined and were mostly above 85%, except 4NC and 5NSA with the average recovery rates of 67% and 82%, respectively, probably due to the absence of EDTA in the methanol (the ranges and the standard deviations of recovery rates can be seen in Table S1). The chemical analysis of the blank samples indicates very low background and rare absorption for 4NC and methyl-nitrocatechols, moderately low background and small absorption for 4NP, methyl-nitrophenols, and nitrosalicylic acids, and notable background and significant absorption for 2,4-dinitrophenol due to the volatility.

3. Calculation and estimation

Because only a portion of the coal combustion smoke was collected, the emission factor of fine particulate NPs (EF_{NPs}) from residential coal combustion was calculated based on the measured emission ratio of NPs to $PM_{2.5}$ and the emission factor of $PM_{2.5}$ reported in the literature (Equation (1)).

$$EF_{NPs} = ER_{NPs/PM2.5} \times EF_{PM2.5} \tag{1}$$

where $ER_{NPs/PM2.5}$ represents the emission ratio of NPs to $PM_{2.5}$ and

$EF_{PM2.5}$ represents the emission factor of $PM_{2.5}$ from each kind of coal. To represent the whole combustion process, the $ER_{NPs/PM2.5}$ used in Equation (1) was the time-weighted average value of the eight samples collected in early and later stages in two repeated combustion experiments. Note that the uncertainty of one set of measurement data is calculated as the standard deviation of the mean. The error propagation method is used here to calculate the uncertainties of emission factors of nitrated phenols from coal combustion with the uncertainties of NP/$PM_{2.5}$ ratios and the uncertainties of $PM_{2.5}$ emission factors.

The EF_{NPs} together with the proportion (i.e., relative popularity) of different categories of residential coal combustion were further used to estimate the total emission amount of fine particulate NPs in China ($Q_{\Sigma NPs}$) as the sum of the emission amounts in each province, as shown in Equation (2).

$$Q_{\sum NPs} = \sum (EF_{NPs} \times C \times P)_{i,j,} \qquad (2)$$

where *C* represents the coal consumption in the residential sector in each province, and *P* represents the proportion of each specific coal type and form. The label *i* indicates three general coal types (lignite, bituminite, and anthracite) and two coal forms (chunk and briquette). The label *j* indicates the 30 provinces of China (excluding Tibet, Hong Kong, Macau, and Taiwan due to lack of data). As for the uncertainty of the emission amount of nitrated phenols, it was calculated with only consideration of the uncertainty of emission factors of nitrated phenols, regarding the coal consumption as accurate values.

4. Results and discussion

4.1. Emission profile of particulate NPs from coal combustion

Based on the measured concentrations of fine particulate NPs, OM, and $PM_{2.5}$ in the coal combustion smoke (data are available in Table S2), the normalized emission profile of NPs from combustion of ten kinds of coal are obtained and shown in Fig. 1. As shown, the emission profile of NPs varied with coal kinds and burning conditions. Overall, 4NC and MNCs (i.e., 4M5NC, 3M6NC, and 3M5NC) were the predominant NPs under most conditions. In the early stage, the combined proportion of 4NC and MNCs exceeded 45% while that of 4NP and MNPs (i.e., 2M4NP and 3M4NP) was below 30% for most kinds of coal. In the later stage, the fractions of 4NP, NSAs (i.e., 3NSA and 5NSA), and 2,4-DNP increased, whereas the proportions of 4M5NC and 3M5NC decreased. Interestingly, the emission profile of nitrated phenols varies with different maturity of coals. The fraction of 4NC and MNCs reaches 51%–81% for lignite, which was much higher than that for bituminite (35%–68%) ($p<0.01$) and anthracite (20%–49%) ($p<0.01$). The proportion of 5NSA was higher for bituminite (11%–27%) than that for other coals ($p<0.05$). Besides, 4NP accounted for 36%–41% of total NPs in anthracite chunk combustion and the fraction was greater than one fourth in the early stage for anthracite briquettes. The emission profiles of NPs from combustion of different coals were to some extent similar to those from biomass burning (Wang et al., 2017a,b), i.e., in most cases 4NC and MNCs dominated the emitted NPs and that occasionally 4NP contributed the largest fraction. It suggests that the coal-derived NPs were likely to be produced from lignin residues in the coal (Bi et al., 2008). Nevertheless, apparent difference also existed that the total fractions of 4NC and MNCs from coal combustion (33%–77%) was lower than those from flaming biomass burning (88%–95%; Wang et al., 2017a,b).

4.2. Emission factors of fine particulate NPs

The emission ratios of fine particulate NPs to $PM_{2.5}$ ($ER_{NPs/PM2.5}$) and to OM ($ER_{NPs/OM}$) for coal combustion were calculated based on their mass concentrations in coal-fired smoke samples (see Tables S3 and S4). Generally, the NPs only accounted for a very small fraction in the fine particulate matter and the organic matter. The $ER_{NPs/PM2.5}$ for individual NPs ranged from 0 to 0.27 $\mu g\,mg^{-1}$, with the $ER_{NPs/PM2.5}$ for total NPs in the range of 0.1–1.1 $\mu g\,mg^{-1}$. The average $ER_{NPs/PM2.5}$ values for chunks of lignite, bituminite and anthracite and for anthracite briquettes were 0.88 ± 0.09, 0.31 ± 0.04, 0.30 ± 0.04, 0.12 ± 0.01 $\mu g\,mg^{-1}$, respectively, which decreased with the maturity of coal. Particularly, we found that the $ER_{NPs/PM2.5}$ values of bituminites with lower volatile matter (LBC and MBC) (0.22–0.30 $\mu g\,mg^{-1}$)

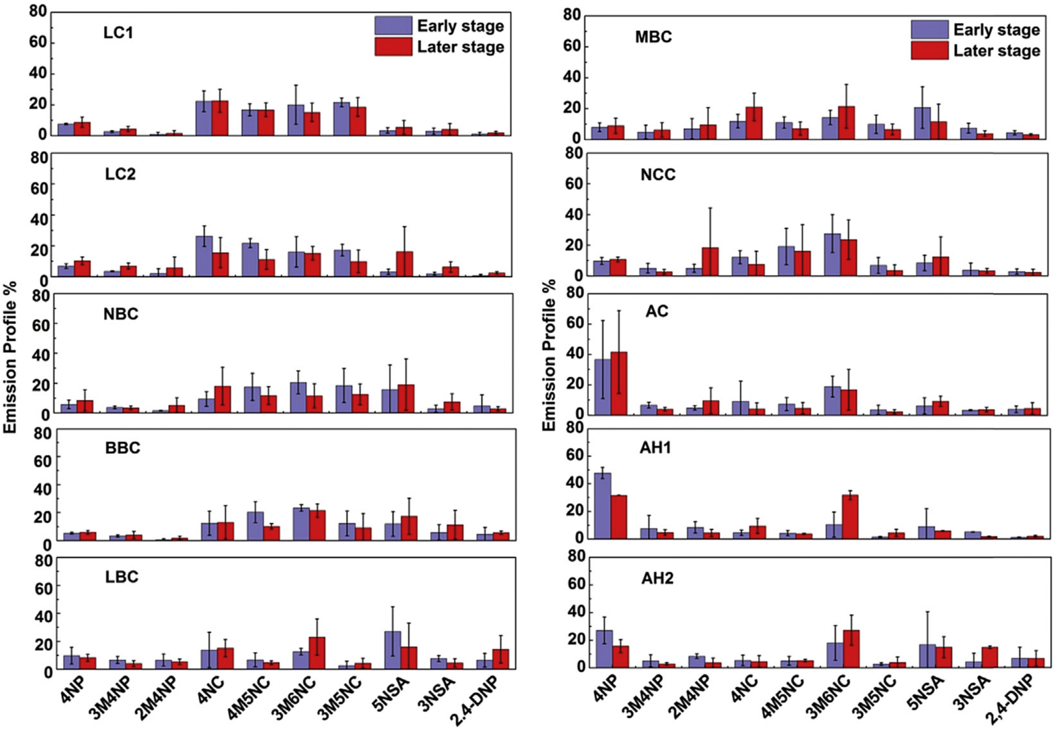

Fig. 1. Emission profiles of NPs in fine particles from coal combustion.

were comparable to that of anthracite (0.27–0.32 $\mu g\,mg^{-1}$) and were much lower than those of bituminites with higher volatile matter (NBC and BBC) (0.28–0.43 $\mu g\,mg^{-1}$) (p<0.05). The above results may be related to that the maturity of LBC and MBC trend towards anthracite and they may have the similar properties with anthracite. In addition, the $ER_{NPs/PM2.5}$ for the anthracite briquette coal was lower than that for the anthracite chunk coal, due to the decrease in the coal fraction and the lignin content with the addition of clays into the briquette coal. The $ER_{NPs/OM}$ for total NPs was in the level of 0.1–3.0 $\mu g\,mg^{-1}$. For four kinds of bituminous coals, the emission ratio of NPs to OM tended to increase when the combustion process changed from early stage to later stage (p < 0.05, as shown in Table S4). The $ER_{NPs/OM}$ from coal combustion was comparable to those from flaming biomass burning, but much higher than those from weakly flaming and smoldering burning of biomass (Wang et al., 2017a,b), possibly due to the relatively high temperature in the flaming burning process of coal and biomass.

The emission factors of fine NPs (EF_{NPs}) from household coal combustion were calculated, based on the time-weighted average emission ratio of NPs to $PM_{2.5}$ for the whole combustion process obtained in this study (shown in Table S5) and the emission factor of $PM_{2.5}$ reported in the literature (on average 0.63–13.2 g kg^{-1} for various coals; Chen et al., 2015; Li et al., 2016; Liu et al., 2007; Shen et al., 2014), due to a lack of whole-sample analysis. Our experiments, including coal, stoves and burning style, were similar to these referred literatures. The EF_{NPs} for natural coke was not included here because the corresponding $EF_{PM2.5}$ was not available. As shown in Table 2 and Table 3, the EF_{NPs} from coal combustion varied with coal kinds. It decreased dramatically with coal maturity and increased slightly when the anthracite chunk was formed into briquette. The estimated EF_{NPs} for chunks of lignite, bituminite, and anthracite and for anthracite briquette were 10.1 ± 3.0 (average ± standard deviation, the same below), 2.3 ± 0.7, 0.2 ± 0.2, and 0.3 ± 0.2 $mg\,kg^{-1}$, respectively. When it comes to individual NPs, the emission factors of 4NC and MNCs ranged from 0.01 to 2.78 $mg\,kg^{-1}$, which were in general higher than other NPs. The emission factors of 4NP and MNPs were moderate (0.01–0.94 $mg\,kg^{-1}$) and those of NSAs and 2,4-DNP were relatively low (0–0.79 $mg\,kg^{-1}$). To our knowledge, the emissions of particulate NPs from coal combustion have not been determined in previous studies, whereas the emissions from biomass burning have been investigated in several studies (e.g., Hoffmann et al., 2007; Iinuma et al., 2007; Wang et al., 2017a,b). The average emission factors of 4NC for pine greens, spruce greens, musasa, Indonesian peat ranged from 0.4 to 4.3 $mg\,kg^{-1}$ (Iinuma et al., 2007). The emission factors of NPs for pine, spruce, grass, and oak were in the range of 0.8–8.1 $mg\,kg^{-1}$ (Hoffmann et al., 2007). The values for leaves, branches, corncob, corn stalk, and wheat straw in flaming burning conditions varied from 0.75 to 11.1 $mg\,kg^{-1}$ (Wang et al., 2017a,b). When compared with the emissions from biomass burning, the emission factors of NPs from coal combustion for lignites and bituminites were comparable or a little higher, while the emission factors for anthracite chunks and anthracite briquettes were lower. The above results suggest that coal combustion could be an important source of fine particulate NPs, due to that large residential coal consumption.

The result that the emission factor of NPs decreased as coal rank increase was primarily ascribed to the difference in the content of phenolic carbon among various coals. Coal originates from biomass and consists mainly of highly condensed aromatic compounds with various functional groups (Whitehurst, 1978). During coal combustion, NPs are likely produced from the reactions between the pyrolysis products which contain phenolic structures, and NO_x (Fuchs and Sandhoff, 1942; Solomon et al., 1993; Yan et al., 2015). The content of phenolic carbon decreases with the maturity of coal (Whitehurst, 1978; Yan et al., 2015), so that lignite emits more NPs than bituminite and anthracite. With regard to the anthracite briquette coal, the addition of a large fraction of clays led to high concentrations of fine particulate matters (shown Table S2) and elevated emission factor of $PM_{2.5}$ (Liu et al.,

Table 2
Emission factors of NPs from residential coal combustion (in mg kg^{-1} except $PM_{2.5}$ emission factor in g kg^{-1}).

Coal	$PM_{2.5}$[a]	4NP	3M4NP	2M4NP	4NC	4M5NC	3M6NC	3M5NC	5NSA	3NSA	2.4-DNP	ΣNPs
LC1	13.2 ± 5.0	0.94 ± 0.37	0.45 ± 0.2	0.17 ± 0.1	2.78 ± 1.22	2.11 ± 0.88	2.07 ± 0.96	2.42 ± 1.02	0.55 ± 0.29	0.41 ± 0.19	0.21 ± 0.09	12.2 ± 4.9
LC2	13.2 ± 5.0	0.71 ± 0.29	0.37 ± 0.15	0.42 ± 0.24	1.68 ± 0.81	1.27 ± 0.66	1.23 ± 0.62	1.05 ± 0.52	0.79 ± 0.37	0.37 ± 0.14	0.15 ± 0.06	8.1 ± 3.4
NBC	7.0 ± 3.9	0.18 ± 0.1	0.14 ± 0.08	0.09 ± 0.06	0.8 ± 0.5	0.42 ± 0.26	0.4 ± 0.23	0.46 ± 0.27	0.38 ± 0.22	0.15 ± 0.09	0.06 ± 0.04	3.0 ± 1.7
BBC	7.0 ± 3.9	0.13 ± 0.07	0.1 ± 0.06	0.04 ± 0.03	0.32 ± 0.22	0.30 ± 0.22	0.47 ± 0.29	0.24 ± 0.19	0.27 ± 0.17	0.15 ± 0.1	0.1 ± 0.06	2.1 ± 1.3
LBC	7.0 ± 3.9	0.18 ± 0.1	0.09 ± 0.05	0.12 ± 0.07	0.49 ± 0.29	0.14 ± 0.08	0.53 ± 0.3	0.17 ± 0.1	0.17 ± 0.1	0.08 ± 0.05	0.51 ± 0.3	2.5 ± 1.4
MBC	7.0 ± 3.9	0.18 ± 0.11	0.12 ± 0.08	0.24 ± 0.17	0.37 ± 0.24	0.09 ± 0.06	0.23 ± 0.13	0.09 ± 0.05	0.11 ± 0.07	0.05 ± 0.03	0.05 ± 0.03	1.5 ± 0.9
AC	0.6 ± 0.6	0.08 ± 0.07	0.01 ± 0.01	0.02 ± 0.02	0.01 ± 0.01	0.01 ± 0.01	0.03 ± 0.03	0.00 ± 0.00	0.01 ± 0.01	0.01 ± 0.01	0.01 ± 0.01	0.2 ± 0.2
AH1	2.2 ± 2.3	0.11 ± 0.11	0.01 ± 0.01	0.02 ± 0.02	0.02 ± 0.02	0.01 ± 0.01	0.06 ± 0.06	0.01 ± 0.01	0.02 ± 0.02	0.01 ± 0.01	0.00 ± 0.00	0.3 ± 0.3
AH2	2.2 ± 2.3	0.05 ± 0.05	0.01 ± 0.01	0.01 ± 0.01	0.01 ± 0.02	0.01 ± 0.01	0.07 ± 0.07	0.01 ± 0.01	0.04 ± 0.04	0.03 ± 0.03	0.02 ± 0.02	0.2 ± 0.3

[a] The values of $EF_{PM2.5}$ from References (Chen et al., 2015; Li et al., 2016; Liu et al., 2007; Shen et al., 2014).

Table 3
Estimated emission factors of NPs in the residential consumption in the year 2016 (1 Tg = 10^{12} g, 1 Mg = 10^{6} g).

Coal type	Coal form	EF_{NPs} mg kg^{-1}	Proportion[a] %	Consumption of coal (Tg)	Emission of NPs (Mg)
Lignite	Chunk	10.1 ± 3.0	4.3[a]	3.31	33.6 ± 9.8
Bituminite	Chunk	2.3 ± 0.7	78.1[a]	60.14	138.3 ± 40.3
Anthracite	Chunk	0.2 ± 0.2	17.6[a]	13.55	2.4 ± 2.7
Anthracite	Briquette	0.3 ± 0.2	100	14.20	3.7 ± 2.7

[a] The proportion of different types and forms for residential consumption from Reference (Chen et al., 2006) and the data of coal consumption from China Energy Statistics Yearbook 2017 (Department of Energy Statistics, China's National Bureau of Statistics, 2017).

2007; Shen et al., 2014; see Table 2), thus the emission factor of NPs for the anthracite briquette coal was higher than that for anthracite chunk coal during combustion process.

4.3. Emission amounts of particulate NPs in China

We further estimated the total emission amounts of fine particulate NPs in the residential sectors in 30 provinces of China in 2016, based on the estimated emission factors, coal consumption, and the proportion of each specific coal type and form. According to data from Chinese Energy Statistical Yearbook 2017, the total coal consumption in the residential sector (including raw coal and briquette coal) in 2016 was 91 Tg (see Table S6). The relative popularities of different types and forms of coal were obtained from the literature and were included in Table 3 (Chen et al., 2006). Finally, the estimated total amount of fine NPs directly emitted from residential coal combustion across China in 2016 was 178 ± 42 Mg. Although the estimated emission amount of fine NPs from coal combustion is less than that from biomass burning (Wang et al., 2017a,b), residential coal combustion is still a very important emission source of NPs in China, particularly in winter when a large amount of additional coal is burnt for heating. Among the 30 provinces, the emission of fine NPs was highest in Hebei, Guizhou, Xinjiang, Hubei, Hunan, Shanxi, Heilongjiang, Yunnan and Shandong (shown in Fig. 2), which are both large consumers and large producers of coal. Particularly, the emission amount of fine NPs in Hebei was much higher than other provinces and accounted for 20% of the total amount in China in 2016. This indicates an urgent need to enforce emission control measures and to promote clean coal utilization in the residential sector. The ongoing actions on reduction in coal use by replacing coal with clean energy such as natural gas and electricity in China also benefit to the emission decrease of nitrated phenols. Note that large uncertainties are implicit in the estimated emission factors and emission amounts of fine particulate NPs in this study, for various reasons: discrepancies in coal composition, stove characteristics, and combustion conditions between the present and previous studies and among actual combustion practices in household coal combustion in different provinces; and the dilution of NPs between chimneys and the atmosphere. Nevertheless, the emission factors and emission amounts obtained in this work indicate the large emission of NPs from coal combustion and provide important basic data for the establishment of an emission inventory and for future atmospheric modeling.

5. Conclusions

In this study, a comprehensively laboratory combustion experiment was conducted to understand the emission characteristics of fine nitrated phenols from residential coal combustion. The emission factor of fine nitrated phenols was calculated according to the average emission ratios of nitrated phenols to $PM_{2.5}$ obtained in this study and the emission factors of $PM_{2.5}$ in the literature. It ranged from 0.2 to 10.1 mg kg^{-1}, decreasing with rising coal rank. The variation of EF_{NPs} with coal rank was attributed to the content of phenolic carbon among

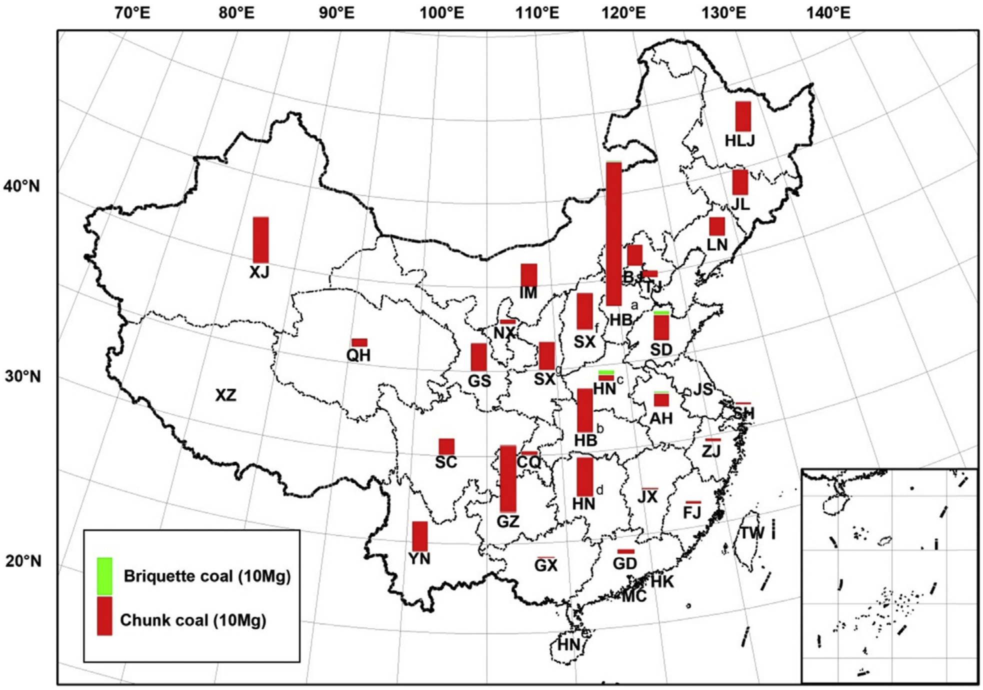

Fig. 2. Estimated emission amounts of fine NPs for residential coal consumption in 30 provinces in China in 2016 (unit in Mg). (HB[a] represents Heibei, HB[b] represents Hubei, HN[c] represents Henan, HN[d] represents Hunan, HN[e] represents Hainan, SX[f] represents Shanxi, SX[g] represents Shaanxi).

various coals. Emission estimation shows that a total of 178 ± 42 Mg fine nitrated phenols were released from residential coal combustion in 30 provinces in China in 2016. The large emission of particulate NPs indicated that more efforts should be made to promote clean coal utilization and to reduce coal use by replacing coal with clean energy in residential sector of China.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests.

Disclaimer

The authors declare no competing financial interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.atmosenv.2019.01.047.

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